# KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM

# **PROCEEDINGS**

## **VOLUME XXIX**

No. 1

President: Prof. F. A. F. C. WENT

Secretary: Prof. L. BOLK

(Translated from: "Verslag van de gewone vergaderingen der Afdeeling Natuurkunde", Vol. XXXIV and XXXV)

### CONTENTS

- H. D. KLOOSTERMAN: "On the expression of positive integers in the form  $ax^2 + by^2 + cz^2 + dt^2$ ". (Communicated by Prof. J. C. KLUYVER), p. 2.
- H. B. DORGELO: "The Duration of the Metastable s<sub>3</sub>- and s<sub>5</sub>-States of Neon". (Communicated by Prof. H. A. LORENTZ), p. 7.
- L. RUTTEN: "On the Origin of the Material of the Neogene Rocks in Java", p. 15.
- WACLAW WERNER and W. H. KEESOM: "The variation of the dielectric constant of liquid and solid hydrogen with temperature", p. 34.
- C. J. VAN DER HORST: "The cerebellum of fishes. 2. The cerebellum of Megalops cyprinoides (Brouss.) and its connections". (Communicated by C. U. ARIËNS KAPPERS), p. 44.
- F. M. JAEGER: "On the Crystalforms of some position-isomeric Dinitrotoluenes", p. 54.
- F. M. JAEGER and P. KOETS: "On Complex Cobaltic Salts with nine-valent lons", p. 59.
- F. A. H. Schreinemakers: "Equilibria in systems, in which phases separated by a semi-permeable membrane". XIII, p. 84.
- H. ZWAARDEMAKER: "The Balance in Radio-physiological Equilibria shifted by l. adrenalin towards the Alpha-side, and by d. adrenalin towards the Beta-side", p. 93.
- J. J. VAN LAAR: "On the Equation of State of Solid Substances (Metals) in connection with their Compressibility and with the Pressure and Temperature Coefficient of this Quantity". (Communicated by Prof. H. A. LORENTZ), p. 95.
- I. LUYTEN, G. JOUSTRA and A. H. BLAAUW: "The results of the temperature-treatment in summer for the Darwin-Tulip". (Second Part). (With one plate), p. 113.
- J. WOLFF: "On a Function which Assumes any Value on a Non-Enumerable Set of Points in any Interval". (Communicated by Prof. R. WEITZENBÖCK), p. 127.
- C. U. ARIËNS KAPPERS: "The relation of the cerebellum weight to the total brainweight in human races and in some animals", p, 129,
- B. L. VAN DER WAERDEN: "Ein algebraisches Kriterium für die Lösbarkeit eines Systems homogener Gleichungen". (Communicated by Prof. R. WEITZENBÖCK), p. 142.
- J. FAUL: "The comparative ontogenetic development of the corpus striatum in reptiles". (Communicated by C. U. ARIËNS KAPPERS), p. 150.
- W. HUREWICZ: "Ueber Schnitte von Punktmengen". (Communicated by Prof. L. E. J. BROUWER), p. 163.
- K. MENGER: "Ueber geodätische Linien in allgemeinen metrischen Räumen". (Communicated by Prof. L. E. J. BROUWER), p. 166.

Mathematics. — "On the expression of positive integers in the form  $ax^2 + by^2 + cz^2 + dt^2$ ")". By H. D. KLOOSTERMAN. (Communicated by Prof. J. C. KLUYVER).

(Communicated at the meeting of October 31, 1925).

In my dissertation (Over het splitsen van geheele positieve getallen in een som van kwadraten, P. NOORDHOFF, Groningen 1924), I have proved an asymptotic formula for the number of representations r(n) of the positive integer n in the form  $a_1$   $x_1^2 + a_2$   $x_2^2 + \ldots + a_s$   $x_s^2$   $(a_1, a_2, \ldots a_s)$  are positive integers) if  $s \ge 5$ . The proof of this formula is merely a direct application of a method, due to HARDY and LITTLEWOOD. This method however does not give at once an asymptotic formula if s = 4, that is to say for the form  $ax^2 + by^2 + cz^2 + dt^2$  (in order to avoid the indices I now write a, b, c, d, x, y, z, t instead of  $a_1, a_2, a_3, a_4, x_1, x_2, x_3, x_4$ ). In this note I give the outline of a method, by means of which it is also possible to prove an asymptotic formula in this case. I write (r, q, v) are integers):

$$S_{\epsilon,q,\nu} = \sum_{j=0}^{q-1} exp\left(\frac{2\pi i r j^2}{q} + \frac{2\pi i \nu j}{q}\right)$$

To every integer p which is prime to q, a number  $p_1$  can be determined by the conditions

$$p(p_1 + N) + 1 \equiv 0 \pmod{q}$$
 ,  $0 < p_1 \leqslant q$ ,

where N is a positive integer. Then the proof of the asymptotic formula depends on the following

Lemma: Let  $n, N, a, b, c, d, \nu_1, \nu_2, \nu_3, \nu_4$  be integers, of which n, N, a, b, c, d are supposed to be > 0. Let  $\mu$  be an integer such that  $0 \le \mu \le q-1$ .

Then, if p runs through those positive numbers which are less than and prime to q and for which also  $p_1 \leq \mu$ , then

$$\left| \sum_{p_1 \leq \mu} S_{ap,q,\nu_1} S_{bp,q,\nu_2} S_{cp,q,\nu_3} S_{dp,q,\nu_4} \exp\left(-\frac{2n \pi i p}{q}\right) \right| < Kq^{2+\frac{7}{8}+\epsilon} (n,q)^{\frac{1}{4}}, \quad (1)$$

where K is a constant, depending on a, b, c, d only (and therefore not depending on q,  $\mu$ , n, N,  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ), (n, q) is the greatest common divisor of n and q and  $\varepsilon$  is an arbitrary small positive number.

<sup>1)</sup> More detailed proofs will be published in the "Acta Mathematica"

The proof of this lemma is difficult and intricate. In the following pages I shall give an outline of the proof of the inequality

$$\left|\sum_{p_1 \leq \mu} exp\left(-\frac{2n\pi ip}{q}\right)\right| < Kq^{\frac{7}{8}+\epsilon} (n,q)^{\frac{1}{4}}, \quad . \quad . \quad . \quad (2)$$

since the essential difficulties are the same as in the case of the more general inequality (1). For the sake of simplicity, I shall suppose N=0, so that

$$pp_1 + 1 \equiv 0 \pmod{q}$$
.

In a  $\xi-\eta$  plane we shall consider the square  $0<\xi\leqslant 1$ ,  $0\leqslant \eta<1$  and in this square we consider the point whose coordinates are  $\xi=\frac{p_1}{q}$ ,  $\eta=\frac{\{np\}}{q}$ , where  $\{np\}$  is the integer, which is  $\equiv np \pmod q$  and for which  $0\leqslant \{np\}\leqslant q-1$ . To every number  $p_1$  lying between 0 and q a corresponding point can be found.

Therefore there are  $\varphi(q)$  points. Let  $N_m$  be the number of these points, which are situated in the rectangular region

$$\frac{m}{M} \leqslant \eta < \frac{m+1}{M}$$
 ,  $0 \leqslant \xi \leqslant \frac{\mu}{q}$ .

where M is a positive integer and m = 0, 1, 2, ..., M-1. Then

$$\sum_{\substack{m \leq \frac{\{np\}}{M} \leq \frac{m+1}{M}: p_1 \leq \mu}} exp\left(-\frac{2n\pi ip}{q}\right) = N_m e^{-\frac{2\pi im}{M}} + O\left(\frac{N_m}{M}\right)$$

and therefore

$$\sum_{p_1 \leq \mu} exp\left(-\frac{2n\pi ip}{q}\right) = \sum_{m=0}^{M-1} N_m e^{-\frac{2\pi im}{M}} + O\left(\frac{\mu}{M}\right). \quad . \quad . \quad (3)$$

It remains to calculate  $N_m$ . In order to do this, we consider the function  $f(\xi, \eta)$  which can be defined as follows:

1. 
$$f(\xi, \eta) = 1, \quad \text{if} \quad \frac{m}{M} < \eta < \frac{m+1}{M}, \quad 0 < \xi < \frac{\mu}{q};$$

- 2.  $f(\xi, \eta) = \frac{1}{2}$  on the boundary of this rectangle;
- 3.  $f(\xi, \eta) = \frac{1}{4}$  in the summits of this rectangle;
- 4.  $f(\xi, \eta) = 0$  in all other points of the square  $0 < \xi \le 1$ ,  $0 \le \eta < 1$ ;
- 5.  $f(\xi, \eta)$  is periodic both in  $\xi$  and  $\eta$ , with period 1.

Then we have

$$N_{m} = \sum_{p} f\left(\frac{p_{1}}{q}, \frac{np}{q}\right) + O(1),$$

<sup>1)</sup> In what follows the letter K denotes a constant, depending on a, b, c, d only. However it does not always denote the same constant.

where p runs through a system of residus  $mod\ q$  and prime to q. The function  $f(\xi,\eta)$  has an analytical expression in the form of a double FOURIER-series:

$$f(\xi,\eta) = \sum_{\alpha=-\infty}^{+\infty} \sum_{\beta=-\infty}^{+\infty} a_{\alpha,\beta} \sum_{p} \exp(2\pi i \xi a + 2\pi i \eta \beta), \quad . \quad . \quad . \quad (4)$$

where

$$\alpha_{\alpha,\beta} = \int_{0}^{1} \int_{0}^{1} f(\xi,\eta) \exp(2\pi i \xi a + 2\pi i \eta \beta) d\xi d\eta.$$

This FOURIER-series is convergent for all values of  $\xi$  and  $\eta$ . We now have

$$N_{m} = \sum_{\alpha=-\infty}^{+\infty} \sum_{\beta=-\infty}^{+\infty} \alpha_{\alpha,\beta} \sum_{p} exp\left(\frac{2\pi i \alpha p_{1}}{q} + \frac{2\pi i \beta n p}{q}\right) + O(1) . \quad (5)$$

Now we can prove

$$\sum_{p} exp\left(\frac{2\pi i a p_1}{q} + \frac{2\pi i \beta n p}{q}\right) = O(q^{\frac{3}{4}} (\beta n, q)^{\frac{1}{4}}) \quad . \quad . \quad (6)$$

We can substitute this in (5). The non-uniform convergence of the FOURIER-series causes some difficulty, which, however, is not serious.

We find

$$N_{m} = \frac{\mu}{Mq} \varphi(q) + O(q^{\frac{3}{4} + \epsilon}(n, q)^{\frac{1}{4}}) \dots (7)$$

for every positive  $\varepsilon$ . The inequality (2) now follows, if we substitute (7) into (3), taking  $M = [q^{\frac{1}{8}}]$ .

The essential idea of the method described, is that the calculation of a sum, where p does not run through a complete system of residus to  $mod\ q$  and prime to q (in fact we had  $p_1 \leq \mu$ ), can be reduced to the calculation of sums, like (6), where p runs through a complete system of residus  $mod\ q$  and prime to q. The proof of (6) is also difficult. It has been proved by LITTLEWOOD in the particular case, where  $(a,q)=(\beta n,q)=1$ . (This proof has not been published). I have succeeded in extending LITTLEWOOD's method for the most general case.

An application of the HARDY-LITTLEWOOD-method making use of the lemma mentioned above, now gives the following result:

$$r(n) = \frac{\pi^2}{\sqrt{abcd}} n S(n) + O(n^{\frac{17}{18} + \varepsilon}) . . . . . . (8)$$

for every positive  $\varepsilon$ , where

$$S(n) = \Sigma A_q$$
,  $A_q = q^{-4} \sum_{q=1}^{\infty} S_{ap,q} S_{bp,q} S_{cp,q} S_{dp,q} \exp\left(-\frac{2n\pi i p}{q}\right)$  (9)

(where  $S_{ap,\,q}$  etc. are GAUSSIAN sums and where p runs through all positive integers less than and prime to q), and S(n) is the singular series.

Before we can conclude, that

$$r(n) = \frac{\pi^2}{\sqrt{abcd}} n S(n) . . . . . . . (10)$$

a detailed examination of the singular series is necessary. For it may happen that S(n) is small for large values of n.

We have

$$A_{qq'} = A_q A_{q'}$$
, if  $(q, q') = 1$ .

Hence

$$S(n) = \Pi \chi_{\overline{\omega}}$$

where the right hand side is an infinite product, where  $\sigma$  runs through all prime numbers and where

$$\chi_{\varpi} = 1 + A_{\varpi} + A_{\varpi^2} + A_{\varpi^3} + \dots$$

The factors  $\chi_{\varpi}$  can be calculated from the second formula (9), by substituting the explicit values of the GAUSSIAN sums.

If we carry out the examination of the singular series in this way, we are led to complicated algebraical calculations, and a large number of special cases have got to be treated separately. Therefore I have carried out the examination for the special case only, where a, b, c and d are odd. Then it is possible to prove

$$S(n) > \frac{K}{\log \log n} > 0$$

if the following conditions are satisfied:

A. There is no prime number which divides three or four of the numbers a, b, c, d.

B. There is no odd prime  $\sigma$ , for which the following relations are true simultaneously

$$\overline{\omega}^2 \mid a, \quad b = \overline{\omega} \ b_1, \quad (b_1, \overline{\omega}) = (c, \overline{\omega}) = (d, \overline{\omega}) = 1, \quad \left(\frac{cd}{\overline{\omega}}\right) (-1)^{\frac{\overline{\omega}-1}{2}} = -1.$$

C. The same for the relations:

$$(c, \varpi) = (d, \varpi) = 1, \quad \varpi^2 \mid a, \quad \varpi^2 \mid b, \quad \left(\frac{cd}{\varpi}\right)(-1)^{\frac{\varpi-1}{2}} = -1.$$

D. The same for the relations:

$$a = \varpi a_1, \quad b = \varpi b_1, \quad (a_1, \varpi) = (b_1, \varpi) = (c, \varpi) = (d, \varpi) = 1,$$

$$\left(\frac{a_1 \ b_1 \ c \ d}{\varpi}\right) = 1, \quad \left(\frac{c \ d}{\varpi}\right) (-1)^{\frac{\varpi - 1}{2}} = -1.$$

E. The same for the relations

$$a+b\equiv 2 \pmod{4}$$
.  $a+c\equiv 2 \pmod{4}$ ,  
 $a+d\equiv 2 \pmod{4}$ ,  $a+b+c+d\equiv 4 \pmod{8}$ .

F. The conditions, that are obtained from B.-E. by permutation of a, b, c, d.

If these conditions are satisfied the formula (10) is true, and therefore we have the following result:

If a, b, c and d are odd and if the conditions A.-F, are fulfilled, then there is only a finite number of integers which can not be written in the form  $ax^2 + by^2 + cz^2 + dt^2$  and the asymptotic behaviour of the number r(n) of representations of the number n is given by (10).

The Hague, October 1925.

Physics. — "The Duration of the Metastable s<sub>3</sub>- and s<sub>5</sub>-states of Neon."

By H. B. DORGELO. (Communicated by Prof. H. A. LORENTZ.)

(Communicated at the meeting of September 26, 1925).

K. W. MEISSNER's 1) researches on the absorption in excited Neon have shown clearly that the  $s_{3}$ - and  $s_{5}$ -states of Neon have a longer duration than the  $s_{2}$ - and  $s_{4}$ -states.

It followed from the theoretical considerations of S. GOUDSMIT <sup>2</sup>) and P. JORDAN <sup>3</sup>) concerning the character of the fundamental term of Neon that the transitions from the  $s_3$ - and  $s_5$ -states to the fundamental state of the atom must be forbidden transitions, hence that the  $s_3$ - and  $s_5$ -states should be considered to be metastable states of the atom.

The investigations of G. Hertz  $^4$ ) and Th. Lyman and F. A. Saunders  $^5$ ) in the extreme ultraviolet have corroborated this view. Only those lines appear that correspond to transitions of the emitting electron from the  $s_2$ - and  $s_4$ -states to the fundamental state. This completely accounts for the results of Meissner in his absorption measurements of excited Neon. For when we have an absorption tube in which the Neon atoms have been brought to the s-states e.g. through discharge, and when these atoms are illuminated by light of a Neon column standing behind it, those of the lines of the principal series of Neon will be absorbed that have the metastable  $s_3$ - and  $s_5$ -states as final level. In the absorption tube the excited atoms will be brought through the light that strikes them from the metastable  $s_3$ - and  $s_5$ -states into the higher-situated p-states.

What has been said is also in harmony with the appearance of self-reversal of the  $2s_5$ —2p and  $2s_3$ —2p lines in a Neon low voltage arc, which can easily be observed by the aid of a Lummer-Gehrcke plate.

In consequence of this self-reversal the Neon low voltage arc gives another distribution of intensity over the lines of the H.S. than that measured by the author for the Neon column <sup>6</sup>). If on one plate with the same time of exposure a photo is taken of the Neon spectrum of a Neon

<sup>1)</sup> K. W. MEISSNER, Ann. d. Phys. 76. 124. 1925 Paschen Festschrift.

<sup>&</sup>lt;sup>2</sup>) S. GOUDSMIT, Physica 5. 70. 1925. Z. f. Phys. 32. 111. 1925.

<sup>3)</sup> P. JORDAN, Z. f. Phys. 31. 877. 1925.

<sup>4)</sup> G. HERTZ, Die Naturwissenschaften 13. 489. 1925. Z. f. Phys. 32. 933. 1925. Physica 5. 189. 1925.

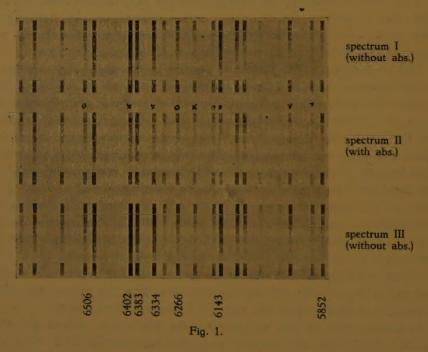
<sup>5)</sup> TH. LYMAN and F. A. SAUNDERS, Phys. Rev. 25. 886. 1925.

<sup>6)</sup> H. B. DORGELO, Physica 5. 90. 1925.

low voltage arc and one of a Neon column, and if the intensities of the sources of light are regulated so that the intensities of the  $2s_4$ —2p and  $2s_2$ —2p are the same in the two photos, the  $2s_5$ —2p and  $2s_3$ —2p lines (especially the stronger lines) of the Neon low voltage arc appear to be fainter than those of the Neon column, which is fully explained by the appearing self-reversal.

In order to examine this absorption by excited Neon more closely, MEISSNER's absorption experiments mentioned before were repeated by me with an arrangement which rendered it possible to measure this absorption quantitatively.

By the aid of the arrangement described already more than once 1), in which a row of light-reducers placed in the path of the light was imaged in a suitable way on the slit of the spectrograph, three photos of the light of a positive Neon column were successively made on one plate with the same time of exposure, which photos are reproduced in fig. 1.



The spectra I and II reproduce the photos of a part of the Neonspectrum of a Neon column, the light of which has traversed the absorption tube, while the excited atoms in this absorption tube have not yet been brought to a state of excitation.

Spectrum II gives the reproduction of the photos of the spectrum of the emission tube, taken while the atoms in the absorption tube were in excited state.

<sup>1)</sup> H. B. DORGELO, Z. f. Phys. 13, 206, 1923, Physica 3, 138, 1923,

Spectra I and III were photographed under identical circumstances, respectively before and after spectrum II to ensure that the emission tube had a constant intensity during the time that the three photos were taken.

Even without measurement of the photos of the spectra the absorption of the  $2s_5$ —2p and  $2s_3$ —2p lines was clear. In the above reproduction the  $s_5p$  combinations are indicated by crosses and the  $s_3p$  combinations by circles. These lines (particularly the stronger ones) are much fainter in spectrum II than in the spectra I and III (compare e.g. the intensity of the line  $\lambda$  6402 with that of  $\lambda$  6383, which is situated immediately beside it). The measurement of these photos rendered quantitative measurements possible, to determine the value of the absorption for the different lines.

We shall not discuss the result of these measurements. We hope soon to publish a more detailed account elsewhere. We will, however, draw attention to a remarkable fact, i.e. that our photos often very clearly (with greater strengths of the current in the absorption tube) showed absorption of the line  $\lambda$  6506, which is a  $s_4p$  combination (in absorption this line  $2s_4$ — $2p_8$  ( $\lambda$  6506) was sometimes reduced to 60% of its original strength). Examined with the Lummer-Gehrcke plate, this line also shows very clearly self-reversal in the low-voltage arc at greater intensities of the current. We shall revert to this result when discussing the results. The  $s_2p$  lines never show an absorption worth mentioning.

This absorption by the atoms in the metastable  $s_5$ - and  $s_3$ -states supplies us with a method to measure the duration of these metastable states  $^1$ ). For as lang as absorption of the  $s_5p$  and  $s_3p$  lines can be observed, it is certain that there are still atoms in the  $s_3$ - and  $s_5$ -state in the absorption tube. When it is ascertained how long after the discharge, which has brought the Neon atoms in the state of excitation, has been interrupted, an absorption tube with excited Neon atoms is still able to absorb the  $s_5p$ -and  $s_3p$ -lines of another discharge tube (to which we always refer as the emission tube), the duration of these states has been determined.

This duration for Neon was determined by us in two ways. The arrangement of the first method is represented in fig. 2.

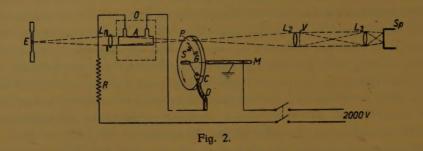
An iron disc S of a diameter of 50 cm., provided with an insulating ring of pertinax is fastened on the axis M of a motor. The disc is placed between emission and absorption tube  $^2$ ) and the spectroscope, and has an

<sup>1)</sup> In principle this method was already indicated by MEISSNER.

K. W. MEISSNER, Ann. d. Phys. 76. 124. 1925.

<sup>2)</sup> As emission tube a straight tube was used with iron electrodes, bore 9,3 mm., Neon pressure 7 mm. The absorption tube was a cylindric tube with side tubes, in which iron electrodes had been placed. At the extremities of the cylindric tube plane-parallel windows were fused in. The Neon pressure in this tube was 8 mm. The tube was exhausted of air at a temperature of 300°, the iron electrodes being exhausted of gas in vacuum. Particular precautions were taken to get the supplied Neon as pure as possible (the Neon still contained a few percentages of He).

aperture G; the pertinax ring is provided with a small brass block C, which is in conductive connection with the axis of the motor, which is



earthed. The excitation of the atoms in the absorption tube takes place. accordingly, during the time that the spring D slides along the brass block C. The arrows in the figure indicate the direction of rotation of the disc. The figure shows the position in which the contact of the brass block C and the spring D is broken. Before, however, the light of the emission tube can pass through the aperture G, the disc must first rotate over a distance a, till the aperture G is in  $P^{-1}$ ). The time between the breaking of the current in the absorption tube and the passage of the light through the opening G depends on the velocity of revolution of the disc and on the distance a. This distance a can still be modified by change of the position of the spring D. It was possible to choose this distance so that with definite velocity of revolution of the disc the light of the emission tube was still absorbed by the atoms which were still in a state of excitation. whereas no trace of absorption was any longer to be perceived with smaller time of revolution. For the line  $\lambda$  6402 (an  $s_5p$  combination) it could visually be judged at what velocity of revolution the absorption disappeared. For the lines that exhibited less absorption the photographic-photometric method was applied by making photos as have been represented in fig. 1 with different velocities of the motor. Of course this requires a good deal of time, but gives more accurate results (also for the line  $\lambda$  6402).

If, therefore, the exact velocity of revolution has been determined at which absorption no longer takes places, the duration can be computed from the number of revolutions of the motor and the ratio of the distance a to the circumference of the circle described by G (160 cm.).

The following table gives some of our observations of the  $s_5$ -state. Hence we see that according to these measurements the duration of the  $s_5$ -state of Neon is about  $\frac{1}{240}$  sec.

In connection with what we already communicated about the line  $2s_4-2p_8$  ( $\lambda$  6506) we may state that at very great velocities of revolution

<sup>1)</sup> The righthand part of the figure represents the usual arrangement for quantitative measurements of the intensity.

TABLE 1.

Distance a	Velocity of revolution of the disc, at which no abs. was any longer to be observed	Duration of the s5-state
9.2 cm.	820 per min.	$\frac{1}{237}$ sec.
20 "	1950 " "	1 260 "
5 "	450 " "	$\frac{1}{240}$ "
8 ,	7.50 " "	1 240 *

this line  $\lambda$  6506 began to show absorption. We shall return to this in the discussion of the results.

The result obtained for the duration of the s<sub>5</sub>-state of Neon was checked by means of another method, which was already indicated in principle by MEISSNER. Though this method must yield less accurate results than that described before, it is worth mentioning by way of control experiment.

The apparatus used is sketched in outline in fig. 3.

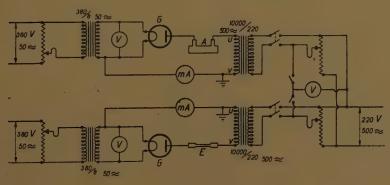


Fig.

By the aid of two rectifiers G one half of a period of a transformed alternating current was sent through the emission tube E, the other half period through the absorption tube. Then the light of the emission tube passes through the absorption tube, when no current passes through the latter. If the duration of the  $s_5$ -state is much smaller than the time of a half period, no absorption is observed; if it is of the same order of magnitude or greater, absorption must be observed.

We had at our disposal a 500-period generator. If the transformed alternating current of this 500-period generator was used the  $s_5p$ -lines showed very strong absorption. It was possible to reduce the number of periods of the generator to 150 periods. Even then the  $s_5p$ -lines presented strong absorption; this means that the duration of the  $s_5$ -state was greater than  $\frac{1}{300}$  sec.

When the transformed alternating current of 50 periods was used, no absorption of the  $s_5p$ -combinations is to be seen, as MEISSNER already stated, and as was also observed by us. We see from this that this method yields as result that the duration of the metastable  $s_5$ -states of Ne lies between  $\frac{1}{100}$  and  $\frac{1}{300}$  second, which is in harmony with the result of the more accurate method discussed first. The first method is more accurate than the second, because in the second it is impossible to say exactly at which moment of the half period the discharge of the tubes sets in, and at which moment the current is again interrupted. All the same it is seen that this method enables us to determine the order of magnitude of the durations.

We have also examined in how far ions left in the absorption tube, might play a part in the results of our measurements. This was especially done in connection with C. ECKARDT's 1) criticism of the measurements of KANNENSTINE 2) and MARSHALL 3), who tried to determine the durations of the metastable states of He and Hg by an entirely different way, but who in reality have probably measured ion ages. With the method followed by us it may be said with certainty that as long as absorption is still observed, the metastable s<sub>5</sub>-states must still be present in the absorption tube. It is, however, possible that these states are formed by recombination of the still remaining ions at or shortly before the moment that the light of the emission tube traverses the disc. That this could, however, not cause the absorption observed, was evident from this that the absorption tube was not luminous at the moment of the transmission of the light of the emission tube through the disc, which can be easily verified by extinguishing the emission tube, and observing with rotating disc from the right whether there was any light to be seen in the absorption tube. For the greater security an absorption tube was made with two side electrodes extra, between which permanently a tension of 100 Volts was laid, which made it possible to remove the ions remaining after breaking of the current of the absorption tube.

With this tube too the same results were obtained as with the preceding one.

<sup>1)</sup> C. ECKARDT, Science 61. 517. 1925.

<sup>2)</sup> KANNENSTINE, Astr. Journ. 55. 345. 1922; 59. 133. 1924.

<sup>3)</sup> MARSHALL, Astr. Journ. 60. 243, 1924.

Discussion of the results.

We mentioned above as result of our measurements that the duration of the  $s_3$ -state of Neon  $\left(\frac{1}{2000} \text{ sec.}\right)$  was shorter than that of the  $s_5$ -state 'P  $\left(\frac{1}{240} \text{ sec.}\right)$ . This result was to be expected. The four s-terms  $s_2$ ,  $s_3$ ,  $s_4$  and  $s_5$  (PASCHEN's notation) and the Hertz—Lyman p-term lie as indicated in fig. 4.

The atoms in the  $s_5$ -state can only return to the p-state through collisions of the second kind, or through

only return to the p-state through collisions of the second kind, or through collisions against the wall or the electrodes of the tube; those of the  $s_3$ -state can, however, also pass into the  $s_4$ -state with small loss of energy through impacts of the second kind,

and from these spontaneously to the ground level.

In particular we will also draw attention here to the behaviour of the  $s_4$ -state mentioned before. We saw there that the  $2s_4$ —2p combinations with greater intensity of the current in the absorption tube show considerable absorption. Analogous phenomena are found in Hg, which we have discussed at length in another communication 1). With absorption of mercury lines through excited mercury vapour the line  $2p_2$ —2s ( $\lambda$  4358) (a combination, therefore, with the non-metastable  $2p_2$ -state) presented stronger absorption than the  $2p_1$ —2s line ( $\lambda$  5461) for greater current densities in the absorption tube.

Following the considerations of Goudsmit <sup>2</sup>) and Hund <sup>3</sup>) concerning the multiplet structure of Neon we believe we may explain the analogous behaviour of the  $2s_4$ —2p combinations of Neon and of the  $2p_2$ —2s combination of mercury partly as follows. In consideration of investigations of Pauli <sup>4</sup>) and Heisenberg <sup>5</sup>) Goudsmit and Hund arrive at the view that the fundamental term of Neon is analogous to a  $^1S_0$  term, the  $s_2$ ,  $s_3$ ,  $s_4$ ,  $s_5$  terms respectively analogous to  $^1P_1$ ,  $^3P_0$ ,  $^3P_1$ , and  $^3P_2$  terms.

According to this view the transition from the  $s_2$  ( $^1P_1$ ) level to the ground level is, however, of an entirely different nature from that of the  $s_4$  ( $^3P_1$ ) level. For the transition  $^1P_1^{-1}S_0$  is then a singulet-line, while the transition  $^3P_1^{-1}S_0$  must then be considered as an inter-combination line, analogous to the line  $1S_2^{-1}P_2$  for mercury.

<sup>1)</sup> H. B. DORGELO, Physica 5. 429. 1925.

<sup>2)</sup> S. GOUDSMIT, Z. f. Phys. 32. 794. 1925.

<sup>3)</sup> F. HUND, Z. f. Phys. 33. 345. 1925.

<sup>4)</sup> W. PAULI, Z. f. Phys. 31. 765. 1925.

<sup>5)</sup> W. HEISENBERG, Z. f. Phys. 32. 841. 1925.

In this way the different behaviour of the  $2s_4$ —2p and that of the  $2s_2$ —2p lines of Neon in absorption through excited Neon atoms has been partly explained, and also the analogous behaviour of the  $2s_4$ —2p combinations for Neon and the  $2p_2$ —2s line for Hg.

It appears also clearly from this that the transitions in inter-combination lines, which must be conceived as disturbance effects according to R. DE L. KRONIG 1), must occur much less readily than the transitions on combination of terms of a same system.

Of course the appearance of the absorption of the  $2s_4$ —2p lines of Neon and of the  $2p_2$ —2s line of Hg is also partly caused by this that the  $s_4$ -state for Ne and the  $2p_2$ -state for Hg are produced respectively from the  $2s_3$ -state of Ne and the  $2p_1$ -state of Hg through impacts of the second kind.

Also the diffusion of the resonance radiation will play a part. The latter, however, also holds for the  $s_2$ -state of Ne. The  $2s_2$ —2p lines of Ne, however, do not show the least absorption, as we saw; hence the part of the diffusion of the resonance radiation will, no doubt, be very small also for the  $s_4$ -state.

Physical Laboratory of the Philips' Glow Lamp Works.

Eindhoven, September 21, 1925.

<sup>1)</sup> R. DE L. KRONIG, Z. f. Phys. 33. 261. 1925.

Geology. — "On the Origin of the Material of the Neogene Rocks in Java."

By L. RUTTEN.

(Communicated at the meeting of September 25, 1925).

When perusing the literature of the last thirty years on the Neogene of Java we are confronted with a fundamental contradiction in the opinions on the composition of the neogene rocks of the island. On the one side authors who have occupied themselves most with the Tertiary of the island (VERBEEK—FENNEMA and MARTIN) hold that the material for the neogene sediments has been supplied exclusively, or nearly so, by the efflata and the detritus of the tertiary volcanoes. On the contrary reports have recently cropped up more and more, stating the occurrence of clastic material, which cannot possibly have been derived from tertiary volcanoes, in the neogene sediments of the island. Some years ago MOLENGRAAFF also advanced the hypothesis that the material of the neogene rocks of Java had originated mainly from the old rocks of the Sunda-land which in the Tertiary lay where the present Java-Sea is situated. Molengraaff, however, started from general postulates and did not substantiate his assertion by facts. It could be expected that a systematic inquiry into the petrographic composition of the neogene sediments in Java might enable us to ascertain which of the two conceptions, alluded to just now, is the right one. Before reporting the results of such an inquiry made by me in the last few months, I will quote some passages from the literature to elucidate the marked contradiction in the various conceptions.

Verbeek and Fennema saw reason to assume that the Neogene in Java had begun with a period of violent volcanic activity ("Old Andesites"); that in the subsequent eras brecciated, marly and limy sediments were formed round the old eruption-centra, which sediments received their clastic material from those same old volcanoes; that during the Neogene volcanic activity became gradually extinct, not to revive again before the transition from the Neogene to the Quaternary and to continue up to the present time. This interpretation of the origin of the clastic material is advocated unreservedly for the rocks of their " $m_1$ ", the oldest division of the Neogene. From page 41 of their book 1) we quote:

"Quant au miocène ancien, il a été appelé par nous étage brècheux, parce qu'il se compose en grande partie de brèches et de conglomérats des roches éruptives.... Cependant il vient s'y ajouter encore un grand nombre d'autres roches, des grès formés de grains d'andésite....".

Of the two more recent divisions of the Neogene the authors do not

<sup>1)</sup> R. VERBEEK et R. FENNEMA, Géologie de Java et Madoura. 1896.

maintain with equal positiveness that they contain exclusively effusive clastic material. However, when considering what the authors write on the composition of the rocks of their  $m_2$  and  $m_3$  section, it appears that they almost always consider that the clastic material originated from the tertiary effusiva  $^1$ ).

1) The following details are given of the composition of the neogene sediments of Java:

p. 53—54.  $(m_2, s, Madura)$ . Lorsqu'on sépare par lévigation la poudre des marnes et des calcaires de la poussière trop ténue, et qu'on porte cette poudre dans du baume de Canada... on s'aperçoit, que, presque dans toutes les roches, se rencontrent des éléments, qui proviennent d'andésites. Ceci devient encore plus évident, lorsqu'on traite d'abord la poudre par l'acide chlorhydrique.... On obtient alors un résidu, qui pour 90 % et parfois davantage se compose de petits fragments de plagioclase.... On trouve en outre des éléments vitreux.... puis encore de l'augite et de la magnétite.... Quelques calcaires renferment un peu de quartz."

p. 144. (miocene limestones from Pasuruan). Les calcaires contiennent en proportion plus ou moins forte.... du gravier d'andésite (petites particules de plagioclase, de pyroxène, de magnétite).

p. 172. (S. Kediri). Dans un petit ravin se trouvent à découvert des couches marneuses... ainsi que des grès d'andésite.

p. 173. (S. Kediri). Le calcaire.... est en partie tendre et marneux, parfois arénacé grace à une proportion assez notable de gravier d'andésite.

p. 206—210. From various parts of Surabaya andesite material from  $m_2$  is mentioned, and never something else.

p. 212. La nature du calcaire de Surabaja est exactement la même que celle de Madura; il est le plus souvent assez tendre et marneux, mélangé de particules d'argile ou de gravier d'andésite.

p. 214. Microscopic description of two marls from Surabaya. Andesite material from these marls is recorded.

p. 238-239. (m3 of N. Rembang). Toutefois il s'en faut de beaucoup que l'étage toute entière soit constituée de calcaire. D'abord une grande partie de la roche est marneuse par suite de la présence de débris d'andésite désaggrégés.

p. 241. ( $m_3$  of N. Rembang). On trouve.... des calcaires.... le plus souvent cependant avec adjonction de gravier d'andésite; il s'y montre aussi deci delà de petits grains de quartz.

p. 243—249. Only Limes and marls with andesite material are reported from the southern zone of Rembang and from North-Madiun. The word quartz does not occur in the descriptions.

p. 261.  $(m_2$  of Madium). Ce sont en grande partie des marnes arénacées, des grès d'andésite calcaires.

p. 262. (Limes from S. Madiun). l'Etage m<sub>3</sub> est constituée en totalité par du calcaire, généralement plus ou moins marneux par addition d'argile et de particules de feldspaths et d'augite.... originaires d'andésite.

p. 272. En Diapara la section  $m_0$  seule des roches miocènes arrive à la surface; elle consiste en calcaire marneux, qui contient encore.... du gravier d'andésite.

p. 288—294. Mention again is made of andesite material in various parts of the marl-zone of Semarang. Only one passage, especially quoted, refers to quartz in the formation: p. 293 "Ces marnes (de Déli pres Ungaran) contiennent... quelques grains de quartz à inclusions liquides, originaires très probablement des grès quartzeux, qui accompagnent constamment les charbons éocènes." (In the vicinity namely detached fragments of glance coal have been found considered to originate from the Eocene).

The subjoined notes show that the authors find in the miocene rocks a considerable quantity of quartz only there where miocene rocks border directly on known Eocene regions (Bagelen, Tji Mandiri) or imagined Eocene regions (Deli near Ungaran, Pekalongan), and that they refer that quartz to the eocene sandstones in the vicinity.

For the rest the only clastic material they meet in the miocene rocks is andesite-débris; traces of quartz are recognized only in limestones from Rembang and from North-Madura 1). It is true, they say that in some unnamed miocene rocks they have identified much quartz, which, however, is very "young" and is derived from quartz-andesites (p. 931—932). Concluding it may be said that the authors consider quartzy sandstones to be characteristic of the Eocene, and sandstones and marls with andesite material of the Neogene.

In his latest comprehensive publication on Java MARTIN also holds the opinion that by far the most clastic material of the neogene sediments originates from tertiary volcanoes, as he says 2):

"Das Material, welches an der Bildung der tertiären Sedimente teilnahm, wurde nach Obigem, während der ganzen Dauer ihres Absatzes in erster Linie von jungen Eruptivmassen geliefert, und daher müssen sich die gleichen petrographischen Charaktere bei Tuffen, Mergeln u. s. w. in den verschiedenen Abteilungen und Stufen der Tertiärformation wiederholen."

True, MARTIN — as is already evident from his first great publication on Java <sup>3</sup>) — was aware that in some rocks from the Neogene many worn quartzes from the "old rocks" occur. In 1880 he ascribes to this even stratigraphical value, in so far as he held the rocks with "old" material

p. 334-338. From various parts of Solo andesite material is recorded.

p. 370-372. Andesite material from the neogene of Djocja is mentioned.

p. 406—410. From  $m_1$  of Bagelen quartz is still mentioned — besides much andesite-material — quartz being derived from the older rocks in the immediate environment; from  $m_2$  mention is made only of andesite-material.

p. 427-428. Also from the neogene of Banjumas only andesite-material is recorded.

p. 441—442. (Pekalongan). Two loose blocks of quartz-sandstone are described, which are held to be eocene, and a limestone with plagioclase and a few quartz-grains.

p. 482. Also from Cheribon only m-rocks with andesite-material are recorded. From Batavia and Krawang nothing remarkable is recorded.

p. 665. (m<sub>2</sub> from Sumedang). Ce sont des grès marneux et des argiles qui consistent en débris plus ou moins altérés de roche éruptive.

p. 665—675. Eruptive material is repeatedly mentioned from the rocks of  $m_2$  west of Bandung, from the region of Bodjong Lopang.

p. 676. (north of Tji Mandiri). Lorsque, du pont construit sur (la Tii Darian) on remonte à l'Ouest jusqu'au plateau, on trouve sur la route des marnes compactes, riches en grains de quartz, provenant de l'éocène.

p. 680—707. From the  $m_2$  region along the Bantam-boundary and from the region along the Southcoast of Preanger only rocks with eruptive material are described.

<sup>1)</sup> My reason for citing so many descriptions from VERBEEK-FENNEMA is that the book has not an index, so that verification takes much time.

<sup>2)</sup> K. MARTIN, Unsere Palaeozologische Kenntn. von Java, Leyden, 1919, p. 9.

<sup>&</sup>lt;sup>2</sup>) K. MARTIN, Die Tertiärschichten auf Java, etc. 1879—1880.

older than those with volcanic material; in his latest publication he has not reverted to this conception. He only mentions 1) in passing the occurrence of much-worn "old" quartzes and derives them from the garnet-bearing schists, which must occur in the deeper underground of Java:

"Der Cycloclypeenkalk aus dem Bette des Tji-Tarum enthält nach Zirkel's Untersuchungen viele Quarzfragmente, welche sich in ihrer Struktur genau so verhalten wie die Quarze in Granit und Gneiss. Das ist von Belang in Verband mit dem, was über die granatführenden Glimmerschiefer mitgeteilt wurde."

In 1908 Mohr 2) has pointed for the first time to the occurence of quartz-material in the  $m_2$ -deposits of the territory of the riverlets Pekatjangan and Merawu in the basin of the Seraju-river. This  $m_2$  consists of "loam-slates" made up of numerous quartz-grains with a colloidal cementing material, of limesandstones and limestone. The quartz-grains in the "loamslates" are averagely 20—50  $\mu$  (maximum 150  $\mu$ ) in diameter; moreover grains of basic plagioclase occur in the "loamslates"; the quartz-grains in the limesandstones have a diameter of 150—200  $\mu$ , (maximum 900  $\mu$ ). Andesite fragments also occur in the lime-sandstone.

In two later publications MOHR's statements are less detailed. In his papers of 1909 and 1910<sup>3</sup>) he writes as follows:

"In het middelmioceen vindt men echter gelaagde gesteenten (zee-afzettingen) met belangrijke hoeveelheid kwarts. Het lijkt mij waarschijnlijk, dat deze gesteenten uit vergruizingsproducten der oergesteenten (graniet en lei) zijn opgebouwd. De jonge kalksteenen eindelijk.... bestaan.... uit.... weinig kwarts" (first part, separate, p. 7).

Regarding the limestone hills in North-Central-Java (Semarang—Surabaya) he states that the limestone is sandy and that the sand consists of quartz with zircon and turmaline. These components are derived from old mountains, such as still occur in Bangka-Billiton, and which are supposed to have lain where now the large row of Javan volcanoes is situated. (5<sup>th</sup> Part. Separate, p. 2). Of the marl-hills between Semarang—Ngawi—Surabaya he next says:

"De hoofdzaak is, dat in de mergels de klei een veel grooter rol speelt en de kwarts veel fijner van korrel is." (5th Part, separate, p. 5).

From a publication of 1911 4) I cite:

pag. 2, 3. "Die Gesteine, die auf Java bodenbildend auftreten, sind nur wenige an der Zahl.... Ausser einigen wenigen Sandsteinen sind die vorhandenen Sedimentärgesteine hauptsächlich jungtertiäre Mergel und Kalke.... Manche (Kalke) sind etwas tonig; die meisten führen mehr oder weniger, gröberen oder feineren Sand. Dieser Sand ist hauptsächlich Quarz; soweit er jedoch Feldspath und Augit ist, oder gewesen ist, kann er verwittern zu Bodenbestandteilen, feiner als obiger Sand."

<sup>1)</sup> K. MARTIN, l. c. 1919, p. 12.

<sup>2)</sup> E. C. J. MOHR, Mededeelingen uitgaande van het Dept. v. Landbouw, 5. 1908.

E. C. J. MOHR, Over den grond van Java. Teysmannia, 1909 and 1910.
 E. C. J. MOHR, Bull. du Dépt. de l'Agriculture XLVII, 1911. Buitenzorg.

p. 48. "Diese (jungtertiären) Sedimente bestehen, wie gesagt, aus Ton und feinem Quarzsand; der Quarz ist genau derselbe wie in den Graniten und grauwackeartigen Sandsteinen von Sumatra, Bangka und Billiton, und Malakka; auch wird er immer begleitet van Zirkon und Turmalin."

A sharper contrast can hardly be imagined than between the conception of Verbeek, Fennema and Martin, who derive the greater part of the clastic material in the Neogene of Java from tertiary volcanoes, and the opinion of Mohr who insists emphatically that the sediments are composed of old-clastic material. It is to be regretted that Mohr has given so little attention to the earlier conceptions, that he never once alluded to this contrast. However, we feel urged to add, that Mohr is not ignorant of the occurrence of volcanic material in the Neogene, but that he does not attach any quantitative value to it.

On page 53 of the last-named publication we find:

"Es versteht sich von selbst, dass auf diesem Mergelrücken (zwischen Surabaja und Semarang).... dann und wann vulkanische Asche niedergefallen ist, und so ist klar dass in dem feinen Sand.... mehr oder weniger Asche.... nachzuweisen ist."

It is not clear whether MOHR means that volcanic ash fell on the marls, after they had been folded and raised (as is suggested by a cursory reading of this passage), or that during the formation of the marls a rain of ashes fell from time to time into the then still existing sea.

In a very recent publication of Mohr 1) we meet with the above conceptions, nearly unmodified, so that I can do without further quotations. Only Mohr points in this work to two possible areas from which the "old" clastic material may have taken its rise: first, old mountains may have been located where at present the volcanoes of Java are situated (See also Mohr 1909—1910); second, the "old" material may be derived from a range of mountains in the Java-Sea or in South-Borneo.

In 1917 and 1918 three publications appeared furnishing information concerning the petrography of the Neogene of Java. L. J. C. VAN Es <sup>2</sup>) describes the Neogene of Bantam, drawing a parallel between this and the Neogene of Palembang, and points out that effusive clastic material occurs as well in the Lower as in the Middle- and Upper-Palembang Strata, as differentiated by him, but that apparently the eruptive force in Bantam has increased gradually towards the conclusion of the Neogene. He also maintains that there are many more indications of acid effusiva (dacites and liparites) in the neogene rocks of Java than one would suspect from Verbeek—Fennema's descriptions. Directly opposite to Bantam seems to be the sediment-petrography of a part of North-Rembang, on which C. W. A. P. 'T HOEN furnishes some information,

<sup>1)</sup> E. C. J. MOHR, De grond van Java en Sumatra, 1922. Amsterdam, p. 8, 73.

<sup>2)</sup> L. VAN ES, Jaarb. Mijnw. on 1915. Verhand. 2. 1917, p. 133 etc.

however without going into the geological consequences 1). In the neighbourhood of Sedan, namely, quartz-bearing sediments seem to have a great distribution in the deeper parts of the Neogene, whereas only in the more recent part of the formation tuffoid sediments appear, which are correlated with the eruptions of G. Lasem, Butak, etc. The quantity of quartz can be so great, that quartz-sands can be collected in the rivervalleys, which is quite a novelty for Java (l. c. p. 254). K. MARTIN had also reported "lime-sandstones" from North-Rembang, but did not study their petrographic structure 2). Finally I myself have recorded in 1917 some details of the Neogene in the region east of Buitenzorg, and have pointed out that in the deeper parts clastic, "old" quartz occurs, while higher up the effusive elements are ever increasing till the Neogene is shut off with true volcanic tuffs 3).

In 1920 K. Ziegler pointed to the occurrence of much effusive material in the Neogene of Java, when describing the Miocene of South-Bantam <sup>4</sup>). Molengraaff <sup>5</sup>) on the other hand insisted in the same year on the presence of "old" clastic material in the Neogene of Java. For, when asking himself where the material in the Neogene of Java and Sumatra comes from, he says:

"But where has one to look for the primary area of denudation L. from where these geosynclinal troughs of Sumatra partly, and of Java entirely have derived the non-volcanic material now found deposited in them? Where, in other words, is to be found the continental area L., to whose shores these geosynclines were marginal? This continental area lay to the northeastward; it is the neogene Sunda-land, etc."

It is evident that MOLENGRAAFF's reasoning is purely theoretical; he did not ascertain to what extent "non-volcanic" material occurs in the Neogene of Java, but considered it as self-evident.

In his dissertation H. Loos <sup>6</sup>) records the occurrence of a number of peculiar minerals in five samples of the soil of Java originating from Pati (residence of Semarang), Tjikalong (res. of Batavia), Kroja, and from the bottom of the Kinderzee. A number of the minerals named in this thesis: and alusite, glaucophane, garnet, turmaline, corundum, topaze, zircon, etc., are undoubtedly derived from "old" rocks, while quartz, which plays an important rôle in all the grounds described, most probably also originates in part from "old" rocks. However, the author does not go into the geological consequences of his finds. Conversely, W. C. Klein has

<sup>1)</sup> C. 'T HOEN, Jaarb. Mijnw. on 1916. Verh. 2e ged. 1918, p. 202-209, 254.

<sup>2)</sup> K. MARTIN, Samml. Geol. Reichsmus. (1). IX. 1912.

<sup>3)</sup> L. RUTTEN, These Proceedings. 1917, p. 670.

<sup>4)</sup> K. ZIEGLER, Jaarb. Mijnw. on 1918. Verh. I. 1920, p. 51 and 59.

<sup>6)</sup> G. MOLENGRAAFF, These Proceedings 23, p. 445-446, 1920.

e) H. LOOS, Bijdr. t. d. kennis van eenige bodemsoorten van Java en Sumatra, Thesis. Wageningen, 1924.

recently pointed out that in a tertiary profile of 3800 m. thickness in Krawang clastic andesitic material plays a prominent part 1).

The examination of about 110 rock-samples from various parts of Java has enabled me to establish some points of agreement in the divergent opinions of the various authors. I may be allowed beforehand to say something about my experimental method. If possible the rock-samples were immediately soaked in water and subsequently washed and sifted; the residue was then examined. This procedure was successful with a number of clay-shales, marls and tuffy sandstones. Lime-sandstones and many limestones were first treated with hydrochloric acid and subsequently sifted while ultimately microscopical sections had to be made of a smaller number of rocks. The object of the microscopical examination was not to determine all the minerals occurring in the rock, but only to ascertain what minerals generally enter into the composition of the clastic material. The siltrests were then first examined in nitrobenzol (n: 1.551), then, if necessary, in a mixture of nitrobenzol and fennel-oil, whose index of refraction was determined (n:1.536) while sometimes they were also examined in fennel-oil (n:1.529), especially when the establishment of the presence of dubious orthoclase was concerned. The results of the investigation have been indicated in two ways: 10. in an "Appendix" all



- Determinable clastic material exclusively "old".
- O Determinable clastic material predominantly "old".
- A Determinable clastic material predominantly "effusive".
- ▲ Determinable clastic material exclusively "effusive".
- 1-110 Newly examined rock-samples (No. 77 and 78 have not been marked on the map).
  - A Shales and lime-sandstones from the Seraju-region (MOHR).
  - B Limestone from the Tji Tarum (MARTIN-ZIRKEL).
  - C Profile of the Tji Kao (KLEIN).

<sup>1)</sup> W. C. KLEIN, Verh, Geol. Mijnb. Genootsch, Nederl, en Koloniën. Geol. Serie. VIII, 1925.

the rocks have been described; 20, on the accompanying map every rock has been marked, four differing signatures being observed, viz. clastic material exclusively "old"; predominantly "old" with effusive admixtures; predominantly effusive with "old" admixtures, and exclusively effusive. The first and the last rubric have of course only relative value, as it may very well be possible that on very close inspection some rocks of the first rubric would still contain traces of effusive material and in some of the last rubric we would still find traces of "old material". It appeared, however, that in practice the division into the four rubrics could very well be carried through. Two rocks, of which the locality could not be established with certainty (no. 77 and 78), are not marked on the map. No more is No. 111, which was examined only when the map was already finished. The rocks examined were procured from different quarters: At my request the pro tem Director of the Research Committee of the Mining Department in the Dutch East-Indies, Dr J. K. VAN GELDER kindly sent me material of 'T HOEN from N. Rembang (Nos. 1—19) and of VAN Es from Bantam (Nos. 100—107). The Bataafsche Petroleum Maatschappij obliged me by supplying, by means of its Administrator at Tjepu, a number of bore-samples from its grounds in N. Rembang (Ledok and Dandangilo) (Nos. 20—32). From Dr A. Tobler I obtained a number of splinters from rocks in the Basel-Museum, presented by many geologists (Nos. 65-78). A number of rocks have been collected in Java by the present writer (Nos. 34—56, 58—64, 81—93, 108—110). The other rocks were in the Geological Institute of Utrecht (Nos. 57, 79, 80, 94—99, 111). My hearty thanks are due to all who assisted me in procuring material. The map also shows the localities of the quartz-bearing marls and sandstones from the Serajubasin indicated by MOHR and of the quartzbearing limestone from the Tji Tarum mentioned by MARTIN. Of course, I could have mapped many more observations i.a. those recorded by VERBEEK—FENNEMA, which I abstained from doing, since it would not alter the picture essentially.

A few items may follow here about the stratigraphical places of origin of the several samples.

'T HOEN'S samples belong to the Older Neogene of the most northern part of Rembang. When we compare the localities of the several samples with the maps and sections of 'T HOEN, it appears that they take up a thickness of 1500 m. in the Tertiary profile. The younger Neogene of a tuffoid nature is not represented.

The Manager of the Bataafsche Petroleum Maatschappij at Tjepu wrote about the boring-samples which he sent:

"De Ledok-monsters representeeren een dikte van 0—550 M. onder de oppervlakte op de culminatie van deze anticlinale. De nummering van 1—7 houdt verband met de toenemende diepte; L. 7 is dus het oudste gesteente.

De met D. 1 gemerkte zak representeert een dikte van 290—412 M. onder de oppervlakte op de culminatie (der Dandangilo anticlinale); D. 2 412—465 M.; D. 3 465—530 M.; D. 4 530—540 M.; D. 5 540—660 M. en D. 6 660—780 M.

Volledigheidshalve deel ik U mede, dat de diepere Ledok-monsters tevens de lagen boven 290 M. op Dandangilo representeeren. (Letter dd. 27 March 1925)."

It appears, then, that the samples examined represent a thickness of about 1200 m. of the Rembang-Neogene, while it is also obvious that among these samples the most recent Neogene cannot be represented as the borings were made at the points of culmination of the intensily denuded anticlines.

The Northern part of Rembang also yielded the numbers 33 (Trembulanticline), 65 (Kedinding-anticline), 66 (Semanggi-anticline), 67—69-(Ledok-anticline); of course, none of these have been derived from the most recent Neogene; further also 70 (Sambiroto), 78 and 98 (Tuban).

A good number of samples originate from the neogene marl-zone between Surabaya and Semarang, partly from the "sand-marls", and partly from the "clay-marls" 1). In this intensily folded area it is difficult to mark the right stratigraphical place of all rocks, but it is safe to say that the various rocks belong to a profile of at least 3000 M. I dare not enter into details concerning the stratigraphical connection between the samples from the marlzone and those from North Rembang. I shall revert to this afterwards. The rocks from the marl-zone are the numbers: 34—56, 58, 59, 62, and 71—74.

Some rocks (Nos. 57, 60, 61, 63, 64) belong to the area between the "marl-zone" and North-Rembang.

The rocks from the area to the east of Buitenzorg (Nos. 81—90) are taken from a profile of a thickness of 3000—4000 M.; of this area many more samples than the ten above-named rocks have been examined by me, but the general picture was not altered by them.

As to the numbers 91-93 from the Tji-Beët-basin we can report as follows: On Verbeek and Fennema's map only  $m_1$  and v (brecciated miocene and quaternary vulcanic formations) are marked. In 1917 I had an opportunity to make some excursions in this district. I, then, found that between the Tji Kundul and the Tji-Beët there occurs a steeply folded formation of 2000-3000 M. thickness inclined southward everywhere or nearly everywhere. Its lower parts contain grey shales, globigerina-marks and sandstones, which remind one forcibly of the older rocks of the neogene marksone Surabaya—Semarang, while higher up more intercalations of volcanic breccias and tuffs gradually appear, to become, in the upper parts, the sole constituents of the formation, so that the upper portion of the formation bears a great resemblance to the "sandmarks" in the East.

Lastly we mention the rocks collected by Van Es in Bantam, originating from Lower-, Middle-, and Upper-Palembang-layers. They also represent a thickness of at least 1000 M. Also here the number of rocks examined is larger than those described in the "Appendix"; also here only some typical rocks were marked in the map.

<sup>1)</sup> L. RUTTEN, Verhand. Geol. Mijnb. Gen. Geol. Serie III. 1916. p. 149-151.

In discussing the results of the examination of the rocks it should be ever borne in mind, that there are many indications that towards the end of the Neogene the eruptive activity in Java has considerably increased. We know this to have been the case in Rembang ('T HOEN l.c.), in the marlzone Semarang—Surabaya (contrast sand- and claymarls), in the Tji-Beët basin (see supra p. 23), in the vicinity of Buitenzorg (RUTTEN l.c. 1917) and in Bantam (VAN Es l.c.). So, whatever the constitution of the Neogene in Java may be, it can a priori be expected that in a number of places a contrast will be perceived between Old- and Young-Neogene, while it is highly improbable that in the Younger Neogene still rocks should be found absolutely free from volcanic material.

Now when looking in the first place at the rocks from N. Rembang, it appears that they hardly ever display traces of effusive material. This applies to the numbers 1-33, and 65-70. Besides organic remains, and sometimes in association with glauconite and pyrite, the silt-residue of these rocks contain, for usual mineral, dusty quartz 1), sometimes with undulatory extinction, which has doubtlessly been derived from "old" rocks. Besides these we also find in them, most often however only in traces: orthoclase, biotite, muscovite, zircon, microcline, andalusite, turmaline and perhaps also epidote (the rare minerals occurring only in a few rocks). Plagioclase, which never has an "andesitic" habitus, occurs very rarely; augite and hornblende are also of rare occurrence. The latter I found only in the rocks 2 and 33; according to a highly esteemed communication from the Bataafsche Petroleum Maatschappij, however, hornblende is sometimes of frequent occurrence in the deeper parts of the Neogene. This uniform petrographic composition seems to be diversified in one respect, namely by the occurrence of coarse-grained rocks (true sandstones, limesandstones with large quartz-grains, etc.) in the North while more southward the sediments are more finely granular, and contain more claymarl. Only in two rocks from North-Rembang (Nos. 78 and 98) did we find exclusively andesitic detritus. The scarcity of effusive material in our samples must in some degree have resulted from the fact that the Younger Neogene is so badly represented. In conclusion we can say that the Older Neogene of Rembang is free from, or poor in effusive material over a thickness of at least 1500 m. and probably over a considerably greater thickness (as it can hardly be imagined that 'T HOEN's profiles and those of LEDOK and DANDANGILO should present exactly the same stratigraphic niveaux). It can further be concluded that the grains of the clastic "old" minerals seem to decrease in size from North to South, and that andesitic material does not occur before the Younger Neogene.

It is of great interest that to the west as well as to the east of North-Rembang some rocks are found containing exclusively "old" minerals as clastic material. They are the rocks 96 from Djapara, 111 from Peka-

<sup>1)</sup> The quartzes originating from the Pretartiary are always rich in inclusions, which gives them a "dusty" appearance.

longan, 95 from Krawang, 86 and 87 from the district N.-E. of Buitenzorg and 76 from the Tji Sadana in the West, and the rocks 57 from Grissee and 77 and 79 from Madura in the East. A sandstone from Bawean also appeared to contain only quartz (N<sup>0</sup>. 99) 1).

To the South of this zone, in Surabaya, Rembang and Semarang a number of rocks have been found which contain either exclusively "old" but finely granular material, (64 from G. Pegat and 63 from Waduk Pridjetan), or besides finely clastic, old material a certain amount of andesitic material, which in these eastern regions of Java is rather basic (no or very little effusive quartz, plagioclases with a mean index of refraction distinctly larger than 1.551, much magnetite, much augite, hypersthene and amphibole). To the latter group belong numbers 61 from G. Girik near Ngimbang, 60 from Kg. Pasinan near Kambangan, 35 from Kedung adem and 73 from Desa Penkul, S. E. of Semarang.

Some of these rocks already belong to the large "marlzone" (35, 60 and 73) which, however, is characterized for the greater part by total absence of "old" material. In most of the rocks of the marl-zone, whether they belong to the younger sand-marls or to the older clay-marls, only remains of basic andesites occur. This applies to the numbers 34, 36—40, 45—48, 50—54, 58, 59, 62, 71, 72 and 74. Only a few rocks of the marl-zone are excepted, either because they contain besides a preponderance of andesitic material also some quartz, or besides a preponderance of quartz also some andesitic material. The major part of these rocks are lying on the north side of the marl-zone (Nos. 41—44, 49, 97). An exception to this is formed by Nos. 55 and 56 from the north-eastern environment of Ngawi.

We have alluded to it that the exact statigraphical relations between the neogene deposits in North-Rembang and those in the marlzone cannot be determined. That does not alter the fact that there are, indeed, some indications. It is known that towards the upper part the sediments of the marlzone are shut off by the Trinil-tuffs of plio-pleistocene age, whereas in the lower parts of the marlzone limestones are frequently met with, although not in a large number. They include Lepidocyclina, so that they are surely to be referred to the Older Neogene. So the sediments of the marlzone, which have a thickness of at least 3000 m., no doubt contain a large part of the Neogene beginning with the older parts, and reaching certainly upwards to the Pliocene 2). But also of North-Rembang we know that the older parts of the Neogene (which, according to 'T HOEN's profiles. have a thickness of at least 2500 m.) must be referred to the Old Miocene, which is proved by the frequent occurrence of Lepidocyclines and even more by K. MARTIN's 3) detailed description of a Mollusca-fauna from these layers. Higher up in this profile effusive sediments begin to

<sup>1)</sup> Among these may also be reckoned the quartz-bearing lime-sandstones from the Kali Wringin, S.W. of Semarang, See: L. RUTTEN. Samml. Leyden (1). X, 1915, p. 2.

<sup>2)</sup> See also R. KOCH, Eclogae geologiae helveticae, XVIII. 2, 1923.

<sup>3)</sup> K. MARTIN, 1. c. 1912.

appear. We may correlate them with the volcanoes of Lasem etc. In the upper tuffs of these Lasem-sediments a fossil flora has been found, according to SCHUSTER already of pleistocene age 1). It may not be amiss, therefore, to compare the upper, volcanic sediments of the Rembang-profile with the "Sand-marls" in the South, and the deeper parts of the Rembang-profile with the clay-marls. Hereby two remarkable contrasts become evident:

- 10. the deeper parts of the Neogene are sandy in the North, sandy-clayey in southern North-Rembang, clayey in the marl-zone, putting aside the volcanic intercalations.
- 20. in the deeper parts of the Neogene in North-Rembang old-clastic material is far preponderant; towards the South this seems to diminish gradually, while it is almost absent in the marlzone. With the volcanic elements it is just the other way about.

In the absence of old-clastic material the following rocks connect up to the rocks of the "marlzone": No. 75 from the marly miocene of Banjumas (also an interesting sediment on account of its considerable amount of Radiolaria); No. 80 from the calcareous miocene of the Djiwomountains in Solo; the rocks from the Tji-Beët-profile (No. 91-93 and many other samples not especially mentioned); the rocks from the S.-Preanger (No. 108-110) and those from Bantam, from different divisions of the Palembang-layers (No. 100—107). Also the rocks from the Tji Kao-valley in Krawang, described by KLEIN (l.c.) may be classed here. Yet still, when I examined the rocks I could detect a difference between East-, and West-Java, in that in East-Java the effusive material has been, as a rule, more basic than in West-Java. Effusive quartz is very rare in East-Java; owing to their greater index of refraction we can almost immediately distinguish the plagioclases in nitrobenzol, consequently they belong to andesine and the still more basic forms; augite, hypersthene, hornblende and ore are mostly numerous. In West-Java, however, effusive quartz is a frequent constituent of the neogene rocks; the plagioclases often have a lower refraction than nitrobenzol and are consequently more acid than andesine; dark silicates and ore are much scarcer. VAN Es (l.c.) has already pointed to this for Bantam, but the same applies to the rocks from the environment of Buitenzorg, to the Tji-Beët-profile and to the S.-Preanger.

For the rocks east of Buitenzorg we refer to the previous conclusion viz. that in their older parts they include much or exclusive old-clastic material, while effusive material occurs increasingly towards the higher parts. It appears that in the north wing of the anticline (see profile RUTTEN l.c. 1917) the old-clastic material occurs in much higher levels than in the southwing.

Somewhat apart from this are the data published by MOHR on the marly

<sup>1)</sup> J. SCHUSTER, Abh. Bayr. Akad. der Wissensch. Math. Phys. Kl. XXV. 6. 1911, p. 51 sqq. 21

miocene to the north of the Seraju and those of MARTIN on the lime-stone of the Tji-Tarum, because a priori we should not expect the old clastic material to preponderate in these sediments. It should be remembered, however, that even now the Eocene and the Pretertiary appear with various quartz-containing rocks not far to the east of the marls in Banjumas, while in the subsoil of the Preanger, in the neighbourhood of the limestone of the Tji Tarum, everywhere eocene quartz-sandstones can be suspected, which, during the formation of the limestones, may have reached the surface for some part and may then have furnished the clastic quartz-material.

It appears that the hypothesis of Verbeek—Fennema that the Neogene of Java is built up exclusively of tertiary volcanic material, as well as Mohr's conception that old-clastic elements occur first and foremost in the Neogene of Java, rest on undue generalization. Three facts can be gathered from the literature and from the examination of a series of neogene rocks of the island. They are:

1. Everywhere in the island volcanic activity increases considerably towards the conclusion of the Neogene.

2. The volcanic forces were apparently aroused much later in the North

than in the South of the island.

3. In the Neogene of the island old-clastic material is of frequent occurrence. Its diminution from the North to the South as to quantity and size of the grains is clearly distinguishable. Very likely also for the most southern marls of the island a considerable part of the finest clay has been derived from the N. and consists of weathering material of old rocks.

Molengraaff's conception, and in some measure also Mohr's, therefore, appears to be correct: from an older mountain-system, presumably to the North of the present Java, a considerable amount of clastic material must have been transported to the South, to such an extent that (anyhow in North-Java) sediments were built up of at least 1500 m. thickness. The minerals yielded by this northern region (viz. especially quartz, orthoclase, zircon, turmaline and andalusite) point to the fact that acid, coarse-grained rocks have undoubtedly been distributed there: the absence of radiolarite in the clastic material implies that the influence of the transporting rivers did not reach Central-Borneo.

#### APPENDIX.

The rocks 1—19 are those received from the Mining-Department. They were collected by C 'T HOEN, engineer, on his exploration in North-Rembang.

No. 1. 't Hoen no. 4 Widodarenriver. White, soft, clayey sandstone with prepon-

derating quartz, with rather much orthoclase and perhaps and alusite.

No. 2. 't Hoen 25 Ta. Kali Gung. Yellow, soft, clayey sandstone. The coarsest fraction of the silt-residue contains much mica partly colourless, partly of a dirty yellow; sometimes distinctly bi-axial, sometimes pseudo-uni-axial. So besides muscovite probably also discoloured biotite occurs. In the finest fraction of silt-

residue we find, besides a paramount abundance of quartz and scanty orthoclase, also some turmaline, rather much long prismatic zircon, a small trace of horn-blende, and possibly andalusite.

No. 3. 't Hoen 41. Watugenuk-river. Yellow-white, soft, sandstone, with a predominance of quartz, a small trace of orthoclase, some microcline and traces of plagioclase, possibly and alusite and epidote. In the coarsest fraction some white mica occurs; zircon is observed in the finest.

No. 4. 't Hoen 100 Ta. River W. of Kg. Gambiran. Yellow, soft, lime-bearing sandstone. The finest silt-fraction contains besides very much quartz a few traces of orthoclase and some zircon.

No. 5. 't Hoen 8. Widodaren-river. Soft, clayey sandstone. In the coarsest silt-residue-fraction much white mica; in the finest besides more than 90% quartz, some orthoclase.

No. 6. 't Hoen 109. Pretjetriver. Grey, yellow-weathering sandy marl. In the thin section the rock appears to be a glauconite-containing Globigerina-marl with much clastic material; the latter contains chiefly quartz, with some weathered biotite.

No. 7. 't Hoen Sentulriver near Tuder. Brown, soft, sandy marl; the clastic material is especially quartz, with possibly some plagioclase.

No. 8 't Hoen, 85c. W. of Watugenukriver. Yellow lime-sandstones with a great deal of quartz, some microcline and weathered biotite.

No. 9. 't Hoen 57. Gemarangriver. Yellow lime-sandstone with traces of plagioclase and augite besides a large preponderance of quartz.

No. 10. 't Hoen 20. Widodarenriver. Lime-sandstone with quartz, some microcline and traces of muscovite.

No. 11. 't Hoen 59. Ta. W. of Panowan. Yellow, sandy marl, in which I found quartz as the only clastic material.

No. 12. 't Hoen 100. Ta. Riverlet S. of Kalidjambe. Yellowish-grey lime-sandstone with much quartz and possibly some orthoclase.

No. 13. 't Hoen 56. Gemarang-river. Limonitic sandstone with traces of orthoclase and microcline besides predominating dusty quartz, sometimes extinguishing undulatorily.

No. 14. 't Hoen 39. Watugenukriver. Brown, limonite-rich lime-sandstone with much quartz and some microcline.

No. 15. 't Hoen 54. North Krindjo. Grey, quartz-bearing lime-sandstone.

No. 16. 't Hoen 89. Ta. N. of Ngrembes. quartz-bearing lime-sandstone.

No. 17. 't Hoen 14. Lombok-river. Yellow, sandy marl-lime with many quartz-splinters.

No. 18. 't Hoen 88 Ta. W. of Ngrembes. Yellow, sandy marl with much glauconite and with quartz, extinguishing undulatorily.

No. 19. 't Hoen 121 Ta. Passar Pamottan near bridge. Sandy, quartz-bearing marl.

The samples 20—26 are boring samples from the Ledok-field in Rembang.

No. 20. Ledok 1. Grey, soft marl. Coarser silt-residue with marl-lumps and Foraminifera; finest silt-residue with quartz and marl-lumps, impregnated with siderite.

No. 21. Ledok 3. Grey soft marl. Coarser silt-rests contain many Foraminifera. Finer with predominating quartz, a little orthoclase and traces of zircon.

No. 22. Ledok 3. Grey, somewhat sandy clay-marl. Coarser silt-rests contain Foraminifera and marl-lumps. Finer silt-rests contain certainly 80 % quartz, besides cather much orthoclase, while a few scattered grains of plagioclase were noted.

No. 23. Ledok 4. Grey, soft marl. Coarser silt-rests with marl-lumps and Foraminitera, finest with microscopic pyrite-concretions and quartz.

No. 24. Ledok 5. Gray, soft marl. Coarser silt-rests are fish-teeth, marl-lumps and

Foraminifera. Finest silt-rests contain marl-lumps, a great deal of quartz, orthoclase, zircon, a few scattered plagioclase and pyrite-concretions.

No. 25. Ledok 6. Gray clay-marl. Coarser silt-residue are chiefly marl-lumps; tinest silt-rests contain besides predominating quartz and marl-lumps rather much orthoclase, limonitized siderite-lumps and fragments of Foraminifera.

No. 26. Ledok 7. Hard lime-sandstone (D. 10033) 1). The lime-sandstone contains a profusion of fine-grained clastic material, quartz prevails by far, besides a great deal of biotite, ragged at the edge, orthoclase (not rare), rare muscovite, zircon. turnaline and a sparse plagioclase.

The rocks 27—32 are boring-samples from the Dandangilo-territory in Rembang. No. 27. Dandangilo 1. Partly soft marl (with marl-lumps, limestone-fragments, muscovite, quartz, orthoclase, and siderite), partly limestones with Lithothamnium and Cycloclypeus.

No. 28. Dandangilo 2. Gray, soft marl (with quartz, orthoclase, zircon, and turmaline), limestone with Cycloclypeus and Lepidocyclina, and lime-sandstone (with pyrite-dust, quartz and some biotite, D. 10032).

No. 29. Dandangilo 3. Lime-marl-concretions and grey, soft marl (with pyrite-, and limonite-lumps, quartz, turmaline, and orthoclase).

No. 30. Dandangilo 4. Limestone-fragments and grey marl (with quartz and zircon).

No. 31. Dandangilo 5. Grey, sandy, soft marl (with Lepidocyclina, Miogypsina and other Foraminifera, with limonite-fragments, marl-lumps, quartz, turmaline, some orthoclase, zircon and pyrite as Foraminifera-filling).

No. 32. Dandangilo 6. Grey claymarl with limestone fragments, very much quartz, rather much orthoclase and some turmaline.

No. 33. is a boring-sample from the territory Trembul in Rembang, presented to me years ago by Prof. Reinhard of Basel. It is a lime-sandstone, in the finest silt-rests of which there is besides much glauconite a profusion of quartz, sparse orthoclase and zircon, some andalusite and traces of green hornblende and magnetite. I did not find plagioclase.

The rocks 34—56 were collected by me on an exploration in the autumn of 1911 between Surabaya and the Solo north of Ngawi.

No. 34. is a volcanic sandstone, between Randegan and Klagen (Surabaya). It contains a profusion of plagioclase, also hornblende, and magnetite.

No. 35. a sandy marl between Kedung adem and Tonda mula; its silt-rests contain besides much plagioclase and hornblende a predominance of quartz.

No. 36. Limestone from G. Silli S. of Tonda Mula. Clastic material very scarce, only plagioclase was demonstrable.

No. 37. a sandy marl, due S. of Djumblang Djati. The only clastic material are andesitic components: plagioclase and hornblende. It may be that some chalcedony is present.

No. 38. Sands N. of Dessa Bengkok with very much plagioclase, with hornblende, augite, and pyrite, the latter constituting a filling of Foraminifera.

No. 39. volcanic tuff with many Globigerinae N. of Dessa Bengkok. Numerous plagioclasse is the only clastic material.

No. 40. clay-marl N. of Losari. The scarce silt-rests contain much plagioclase and also chalcedony.

No. 41. Limestone summit G. Dantjeh contains besides plagioclase (not scarce) and hornblende very much quartz.

No. 42. Limestone, S.-W. of Temajang, contains besides preponderating quartz a little plagicalese and amphibole, and some magnetite.

<sup>1)</sup> The D. numbers refer to the collection of microscopic sections in the Geol. Institute of Utrecht.

No. 43, sandy marl N. of Gangsem, S. Rembang contains much plagioclase and

hornblende; also some quartz.

No. 44, sandy marl S. E. of Temajang, S. Rembang contains besides numerous plagioclase, hornblende and andesite-groundmass also still numerous quartz, with a few zircon-needles.

No. 45. Limesandstones between Kalipang and Glidah, S. Rembang consists of 2 samples with andesitic material (hornblende and plagioclase), sponge-spicules and newly formed chalcedony.

No. 46. Kalipang, North Kediri, lime-sandstone, contains clastic material (very much plagioclase and hornblende) and also augite. I could not detect "Old" materials.

No. 47. S. of Klampoq, S. Rembang is a lime-sandstone with much plagioclase, hornblende and opal; "old" material is lacking.

No. 48. N. of Klampoq, S. Rembang is a lime-sandstone with plagioclase, hornblende and magnetite, in which I did not find "old" material.

No. 49. S. of Desa Brabo, S. Rembang is a marly sandstone, with some quartz besides plagioclase and hornblende.

No. 50. S. of Tawaran, S. Rembang is a lime-sandstone with plagioclase, augite and hypersthene.

No. 51. G. Ngantjik, S. Rembang sandy marl between clay-marls; contains only andesitic material (plagioclase, hornblende, magnetite).

No. 52. N. of Kali Dandang, S. Rembang, impure limestone with sponge spicules and plagioclase.

No. 53. S. of Ngraho, S. Rembang, sand-layer between clay-marls, contains andesite material, plagioclase far predominating.

No. 54. N. of Pritjet, S. Rembang, sandlayer in clay-marls with plagioclase and hypersthene.

No. 55. S. of Kedung Pasir, S. Rembang. Lime-sandstone with much andesitic material, but also rather much, old-looking quartz.

No. 56. N. of Ngawi, N. Madiun. Lime-sandstone with more quartz than andesitic material.

No. 57. a marly lime-stone on the road from Grissee to Girik (near Surabaya), collected by Prof. Wichmann. It contains very scarce material, insoluble in hydrochloric acid, among which I can distinguish besides limonite-lumps only splinters of quartz.

The numbers 58-64 have been collected by me on a visit in 1910 to the environment of Ngimbang, residence of Surabaya.

No. 58. sand-marl from D. Garung, S. E. of Ngimbang, contains typical andesitic débris: magnetite, plagioclase, hornblende and hypersthene.

No. 59. foraminifera-bearing sandmarl from G. Wedon, S. of Sukarame, contains besides plagioclase, hornblende, and magnetite also fragments of andesite-groundmass.

No. 60. East of Desa Pasinan, south of Kambangan is a blue claymarl with much pyrite-dust, with quartz and a little plagioclase.

No. 61. N.-W. of G. Girik near Ngimbang a blue claymarl with much quartz and with zircon, but also with magnetite, plagioclase and hornblende.

No. 62. waterfall near Kabuh is a sandmarl with exclusive andestic material.

No. 63 from Waduk Pridjetan north of Ngimbang, is a spherical, calcareous concretion; the clastic material is at least 90% "old" quartz and besides some orthoclase, zircon and possibly andalusite.

No. 64. G. Pegat near Babat is a limestone, whose extremely scarce clastic constituents are exclusively "old" material; besides at least 95 % quartz only some limonite and a few pumice needles occur.

Through the kind mediation of Dr. A. TOBLER I received a number of rocks from the Neogene of Java from the Museum of Basel. They are described below (nos. 65-78); of the numbers 77 and 78 I could not mark the exact localities on the accompagnying map.

No. 65. (BLUMENTAL 17) is a boring sample from the boring-field Kedinding in N. Rembang. The very scarce silt-rests consist of predominating quartz, a little orthoclase, some zircon and muscovite.

No. 66. (BLUMENTAL 11) is a boring-sample from the territory of Semanggi in North Rembang. The silt-rests of this marl consist of a great deal of quartz, some orthoclase, rather much pyrite or limonitized pyrite, while a single plagioclase was found.

No. 67—69. originate from the Ledok-territory in Rembang. No. 67. (HOTZ 41) is a soft marl; silt-rests contain very much quartz, rather much orthoclase and muscovite, some plagioclase and zircon, and unmistakable andalusite. No. 68 (HOTZ 39) is a hard brownish-grey lime-sandstone; it contains besides Globigerinae rather much fine-grained clastic material, with predominating quartz, some muscovite and a very rare plagioclase. No. 69 (Blumental 14) is a glauconitic lime-stone with many Foraminiferae. Clastic constituents were frequently occurring quartz and a single orthoclase.

No. 70. (ERB 3) from Sambiroto near Sedan. The coarse silt-rests are above all fossil-fragments. The finest silt-rests are rather varied: besides quartz as the chief constituent, there occur orthoclase, and alusite, microcline, zircon, and perhaps epidote.

No. 71. (HOTZ 61) from Sambung near Gedangan, S. Semarang is a Globigerinalimestone with little clastic material, among which only fresh splinters of plagioclase could be identified.

No. 72. (HOTZ 78) North of Desa Truka, N. E. of Salatiga is a Globigerina-marl, in which the only clastic material is andesitic plagioclase.

No. 73. (HOTZ 63), greyish-white lime-sandstone from Desa Penkul S. E. of Sema-rang, contains besides much quartz a small amount of andesitic plagioclase.

No. 74. (HOTZ 53), between Grogol and Djetis, N. Solo is a hard, sandy lime-stone with Foraminiferae, among which Lepidocyclinae. Only andesitic material was found in it, notably much plagioclase of zonary structure and a little hornblende and augite.

No. 75. (REINHARDT 7), from Kali Tandjung near Gambarsari, Banjumas is a whitish-grey, tuffoid rock. It is very fine-grained, little limy and contains besides scarce Globigerinae and Pulvinulinae many Radiolariae and a few sponge spicules. The only clastic material I could detect with certainty were some plagioclases with andesitic habitus.

No. 76. (REINHARDT 4), grey, marly, glauconitic Cycloclypeus-lime from Pagutan on the Tji Sadana, Batavia, bearing rather much glauconite. The only fine-clastic material I could recognize was quartz.

No. 77. (TOBLER 54) from Ajer mata in Madura is a limestone with very many unmistakable quartz-splinters.

No. 78. (REINHARDT 9), S. of Kapo Kidul, between Babat and Rembang is the filling of an Arca in which typical andesitic material occurs: much plagioclase and pyroxene, which is chiefly hypersthene.

The following two numbers were in the Geol. Institute of Utrecht.

No. 79. grey, finely stratified, marly sandstone from Durdjan, distr. of Sapulu, Madura, contains on the planes of stratification much muscovite and carbonaceous scales. In the silt-rests besides much quartz, some chlorite and muscovite and also orthoclase appears.

No. 80. from G. Tulu, Djiwo Mountains, S. of Klaten, is a limestone with sponge spicules and much andesitic plagioclase and amphibole.

The numbers 81—90 were collected by me in the district east of Buitenzorg.

No. 81. from the Tji Keas, is a clay-shale, in which quartz does not occur; in the roof and the floor andesitic tuffs occur.

No. 82. from the Tji-Bedug, a sideriver of the Kji Keas, comprises two rocks: a clay-shale, on which there are lumps of chalcedony and scarce, pellucid, untwinned plagioclases with refraction-indices lower than 1.551, and a lime-sandstone with numerous plagioclases, fragments of ground-mass and scarce biotites (which no doubt have been phenocrists), rather frequent splinters of quartz, clear as water, which has undoubtedly originated from quartz-phenocrists. It appears, then, that in this lime-sandstone we have to do with material from a dacite. (D. 10075).

No. 83. (D. 10050) from the Upper-Tji Teureup is a silicious clay with very numerous but mostly very small splinters of cloudy quartz. It contains, moreover, musco-

vite scales. I did not find any plagioclase.

No. 84. S. E. of Tjiluwar is a clay-shale, whose silt-rests are composed of much limonite, and silicified lumps and of extremely scarce plagioclases and some dusty

quartz.

No. 85. (D. 10059) from the Tji Teureup, W. of G. Pantjar is a grey lime-sandstone with traces of carbon laminae. The clastic material appears to be almost exclusively quartz and grains of siliceous aggregate; besides some traces of muscovite and plagioclase with non-andesitic habitus occur.

No. 86. (D. 10060), S. of Kelapa Nungal is a yellow Amphistegina-limestone with

traces of dusty quartz, sometimes with undulatory extinction.

No. 87. (D. 10063), S. of Kelapa Nungal is a Cycloclypeus limestone with quartz-splinters.

No. 88. (D. 10063), S. of Kelapa Nungal is a Cycloclypeus limestone with quartz, is somewhat glauconitic. The clastic material consists exclusively of dusty quartz, often in sharp splinters, which sometimes extinguish undulatorily.

No. 89. A sandy layer in clay-shale, W. of G Karang, contains as clastic material predominating, pellucid, sparsely twinned plagioclases with an index of refraction

of about 1.546; besides some dusty quartz occurs.

No. 90. (D. 10065), W. of G. Karang to the south of no. 89 and from greater depth of the profile is a greyish-brown, slightly limonitic quartz sandstone, containing clastic material consisting exclusively of splinters and grains of dusty quartz.

The number 91—93 originate from the basin of the Tji Beët in the north-western corner of the Preanger Regencies.

No. 91. from the Tji Petjung, side-river of the Upper Tji Beët is a Globigerina marl, reminding us of the Central- to East-Java marls from " $m_2$ ". The clastic material it contains, is besides one or two zircons exclusively plagicalese, clear as water, slightly twinned, with an index of refraction of about 1.545. In the large disclosure also grey, hard clay-shales and sandstones occurred; the strike was N 85 W with a south dip of  $60^{\circ}$ .

No. 92. South of the Tji-Beët (strike N. 70.0 dip. 60° S.) is a yellow, tuffy sandstone, containing pellucid plagioclase, chalcedony-lumps and quartz clear as water and undoubtedly effusive.

No. 93. is a white, tuffy sandstone S. of the Tji Beët with much opal, magnetite, and slightly twinned plagioclase (n. about 1.551), and with little hornblende and hypersthene.

The numbers 94—99 are in the Geol. Inst. of Utrecht.

No. 94. Limestone from Pangkalan, distr. of Tegalwaru (Krawang) contains very scarce silt-rests, among which pyrite formed in situ in microscopic concretions, and a few plagioclases, clear as water and with refraction indices between 1.545 and 1.551.

No. 95. Limestone from the waterfall of Tjikombang, distr. of Darandang (Krawang). Among the silt-rests we see besides zircons far prevailing old quartzes and fragments of siliceous aggregates.

No. 96. Limestone from Kali Kebolintang near Tjiluwak, Djapara, contains rather

many silt-rests, consisting chiefly of old quartz, some orthoclase and aggregates of silicic acid.

No. 97. from Telawa, residency of Semarang is a limestone with much plagioclase, some hornblende and some old quartz.

No. 98. from Tuban, N. Rembang is a limestone with much plagioclase, a little augite and magnetite.

No. 99. from Bawean (S.W. of Gg. Kelumpang) is a white sandstone, containing much dusty quartz. No "effusive" minerals could be demonstrated in it.

The numbers 100—107 were collected in Bantam by L. J.C. VAN ES, mining engineer.

No. 100. from the Upper Palembang-layers of the Tji Lajang (VAN ES 124) is a grey, tuffoid sandstone, in which only young, effusive material was found.

No. 101. (VAN ES 127) from the Mid-Palembang-layers of the Tji Lajang is a green, tuffy sandstone, containing exclusively effusive material, notably much magnetite, much felspar, and some quartz which is clear as water and decidedly effusive.

No. 102. (VAN ES 128) from the Mid-Palembang-layers of the Tji Lajang is a white, fine-grained, sandy rock, with much opal, many lumps of silicic-acid aggregate, fairly much plagioclase (n about 1.551), a little pyrite and effusive quartz: it is a typical dacitic mineral.

No. 103. (VAN Es 129a), from the Mid-Palembang-layers of the Tji Lajang is a greenish yellow, partly clayey, tuffy sandstone with much felspar (n about 1.551) and with pyrite.

No. 104. (VAN ES) from the Tji Muli between Desa Tji Muli and Tjurung-dalung (Mid-Palembang-layers) is a tuffy marl with much effusive felspar and travelled silicic acid-lumps.

No. 105. (VAN ES 104a) from the Tji Muli near Desa Tjiwahaju (Lower Palembang-layers) is a grey, tuffy rock with scarce, pellucid, decidedly effusive quartzes, with pyrite, and with much plagioclase, the index of refraction being  $\pm$  1.551. Also here the clastic material is of dacitic nature.

No. 106. (VAN ES 43) from Tji Majang hilir is a grey, clayey-sandy rock, with much felspar (n 1.545—1.551), and with lumps of silicic acid-aggregate.

No. 107. (VAN ES 193) from the Tji Minjak below Barengkok, Mid-Pal. L., is a tuffy sandstone with magnetite and plagioclase.

The numbers 108—110 were collected by me in S. Preanger in 1912.

No. 108. a grey marl S. of Bodjong Lopang, contains besides decidedly effusive material a few grains of quartz, which is probably "old".

No. 109. a marine tuff found north of Sagaranten, contains exclusively effusive material, and especially plagioclase and magnetite.

No. 110. a marine, tuffy marl S.W. of Sagaranten contains also exclusively effusive material: magnetite and plagioclase.

No. 111. from Muntiradja in the K. Genteng (Pekalongan) is a Lepidocyclina-lime with a few grains of dusty quartz. It may be it also contains traces of young effusive material.

Utrecht, September 1925.

Physics. — "The variation of the dielectric constant of liquid and solid hydrogen with temperature." By WACLAW WERNER and W. H. KEESOM. (Communication No. 178a from the Physical Laboratory at Leiden.)

(Communicated at the meeting of September 26, 1925).

- § 1. Introduction. The dielectric constant of liquid hydrogen was measured provisionally at Leyden by Breit and Kamerlingh Onnes 1), after that by Wolfke and Kamerlingh Onnes 2). The latter extended their investigations to solid hydrogen and investigated also the variation of the dielectric constant with temperature. However, as they themselves say, the measurements at lower temperatures are not of the same accuracy as those at the boiling-point of hydrogen. The question, how the dielectric constant varies with temperature is however of so much importance, that it appeared to us worth while to repeat the measurements with greater accuracy.
- § 2. Method. We followed the same method as WOLFKE and KAMERLINGH ONNES; the apparatus was also the same, except in some details where improvements were made. So, for the description, we refer to the communication mentioned.

The sensitivity and accuracy of the method of measuring is limited particularly by the difficulty of keeping constant during a long time the frequency and the intensity of the electric oscillations, which are maintained in the primary circuit by means of a triode-lamp 3). For this the constancy of the temperature of the lamp, and particularly that of the incandescent cathode, is essential. Constancy of the heating current was obtained by using accumulators of great capacity (130 A.h.) and by often changing them, and also by soldering all junctions in the primary circuit.

In spite of this there were still continuous changes of the frequency, which seemed to be intimately connected with the temperature of the

<sup>1)</sup> G. Breit and H. Kamerlingh Onnes. These Proceedings 27, 617, 1924, Leiden Comm. No. 171a.

<sup>&</sup>lt;sup>2</sup>) M. WOLFKE and H. KAMERLINGH ONNES. These Proceedings 27, 627, 1924, Leiden Comm. No. 171c. Spraw. i pr. Warsz. Tow. Polit. III. 7, 1924,

<sup>&</sup>lt;sup>3</sup>) Comp. i.a. J. HERWEG, Verh. d. D. Physik. Ges. 21, 572, 1919. W. H. ECCLES & J. H. VINCENT, Proc. Roy. Soc. A 96, 455, 1919. M. H. BELZ. Phil. Mag. 44, 479, 1922.

environment. They were finally greatly reduced, by covering the triodelamp with a metal mantle, through which a current of water was circulated. By regulating this current a possible still remaining tendency to a change in the frequency could be compensated. Small irregular jumps, however, we could not entirely eliminate.

The sensitiveness of the method is strongly influenced by the steepness of the resonance curve. Owing to the considerable resistance (42  $\Omega$ ) of the vacuum thermoelement, this curve was rather flat. To improve this, we applied a pretty strong coupling (distance between the both self-induction-spirals 8 cm.). Owing to the beats so caused in the secondary circuit there appear two maxima in the resonance curve. Between these maxima there is a part of the curve, which is much steeper than the extreme parts. If during all the measurements only the same branch is used, there is no objection to using a stronger coupling, as it is here only necessary to have the same conditions before and after switching in the experimental-condenser.

The sensitivity of the measurement was 7 to 20 cm. in the galvanometer deflection per 1 mm. reading of the measuring condenser. This could be observed to  $\frac{1}{4}$  mm., which amounts to 1/5000 of the measured capacity. In order to obtain this accuracy it was necessary to calibrate the scale by means of an additional condenser of constant capacity. The values of the dielectric constant, thus corrected, were always greater than the uncorrected values by an amount of 0.0015 to 0.0021.

In order to obtain greater constancy we changed later the scale, that was gummed on card-board, for a scale engraved on a polished nickel-plate. The series III and IV of our measurements were made with the latter scale. The scale was bent in a solid, wooden frame to a circular arc with a radius of 1.5 M. In the centre of this arc was the mirror which was fixed to the axis of the measuring condenser. By means of a telescope we adjusted to whole millimeters of the scale, which was illuminated properly and we controled the adjustment to 0.1 mm. The new scale was calibrated in the same way as the old.

§ 3. The experimental condenser. The arrangement of the condenser and of the cryostat, in which the condenser was mounted, was the same as used by Wolfke and Kamerlingh Onnes. As, however, the glass rod, to which the parts of the condenser were affixed, broke several times owing to the strong refrigeration, we fixed those parts to the rod by means of iron pieces. As the rod broke several times, we obtained different series of measurements. For each series there is a different value for the capacity, which was constant for that series.

The small cap which served for current supply to the condenser, was furnished with a silver plate which gave a good contact.

The pressure of the hydrogen in the condenser, just as the pressure of the hydrogen in the cryostat, could be read on manometers.

§ 4. The programme of the measurements was as follows: 10. measurement of the capacity in liquid hydrogen at atmospheric pressure; 20. at reduced pressure, the observations on both manometers having become stationary; 30. measurement of the capacity after the inner vessel had been emptied, the bath being brought again to the temperature of hydrogen, boiling under atmospheric pressure. In some cases this measurement had to be replaced by a measurement at room-temperature on the following day. This measurement served to control that there had been no change of the capacity owing to some injury. Each measurement of the capacity consisted of 5 to 6 separate measurements. When there were disturbing changes in the vibration-circuit or when points were investigated, that were near to each other, this number was reduced to 4 or 3. Each capacity-measurement took 34 to 2 hours.

The separate measurement consisted of 7 successive adjustments of the measuring-condenser with no current in the galvanometer circuit, the experimental condenser being alternately switched on and off.

The results of the separate measurements often differed more from each other than corresponds to the accuracy expected. Besides the accidental observation-errors there were apparently still other unexpected sources of error.

The wave-length used was about 500 M. By changing from 300 to 600 M. no influence of a change in wavelength could be observed.

We then obtained the dielectric constant from the ratio between the capacities of the condenser filled and empty. A correction was made for the capacity of the little supply-cap 1).

§ 5. Temperature and density of the hydrogen. The temperature of the liquid hydrogen was derived from the pressure of the saturated hydrogen-vapour according to the formula of Verschaffelt  $^2$ ); for solid hydrogen the temperature was interpolated from the data of Simon  $^3$ ). The pressure in the innertube  $p_i$  and also the temperature in the innertube  $T_i$ , were always somewhat higher than the values  $p_e$  and  $T_e$  of the cryostatbath. The difference is 0.10 degrees, at the boilingpoint, 0.35 degrees at the meltingpoint, and was even 0.7 to 0.9 degrees for solid hydrogen. This difference is to be ascribed to the radiation, which penetrated through the slits in the silvering of the vacuumvessels, into the innertube, and which was absorbed by the metal of the condenser. The temperature can be considered as being sufficiently uniform (because of the small thickness of the liquid-layers (0.2 cm.) between the vertical condenser plates).

A possible doubt whether the pressure of the hydrogen-vapour in the

<sup>1)</sup> The capacity of the little cap in liquid hydrogen is 0.46, the correction to the D.C. being 0.0006 for liquid, and 0.0005 for solid hydrogen.

<sup>2)</sup> J. PALACIOS MARTINEZ et H. KAMERLINGH ONNES. Arch. Néerl., sér. IllA, 6, 31, 1923. Leiden Comm. Nº. 156b.

<sup>&</sup>lt;sup>3</sup>) F. Simon, Z.S. f. Phys. 15, 307, 1923.

innertube really corresponds to the temperature of the liquid, can be avoided by the observation, that for a pressure of 5.7 to 5.6 cm. the capacity changed rapidly, which indicates that at this pressure the hydrogen is becoming solid. This corresponds approximately to the value of the triple point-pressure of hydrogen obtained formerly 1) 2).

The densities were interpolated from the data of MATHIAS, CROMMELIN and KAMERLINGH ONNES 3). Below 14°.8 K. we had to extrapolate.

• § 6. Accuracy of the method. The mean error of a separate measurement, derived from the values obtained at the different adjustments of which it consisted (see § 4), varied from 0.003 % to 0.03 % with a mean value 0.015 %. The differences between the separate measurements had a mean value of 0.06 %. If we calculate the mean error of the final result of a series of measurements from the deviations of all numbers from that final result, we obtain a mean error of 0.02 %. This gives for the dielectric constant an error of 0.04 %, which means for liquid hydrogen an uncertainty of 0.0005.

The measurements at the boilingpoint of hydrogen (table III) confirm this estimation.

They were made on different days: also the capacity of the empty condenser was different. The results differ by not more than 0.0005 from the mean value.

The relative values of the results can be considered as being accurate to  $^{1}/_{25}$ %. For judging the absolute values we must also consider the capacity of the supply-cap, by which the uncertainty is still increased by 0.0002 at the most.

The pressures were read to 1 mm., which corresponds to an accuracy of 0.01° for liquid hydrogen. For solid hydrogen, for which the pressures could not be kept so constant, the accuracy of the temperature is not more than 0.1°.

§ 7. Results. The results of the measurements are given in table I. Column I gives the capacity of the condenser  $C_{H_2}$ , filled with liquid or solid hydrogen, column 9 that of the empty condenser  $C_V$ . In 10 are given the values of the dielectric constant calculated from 8 and 9, in 11 the values corrected according to the capacity of the supply-cap.

<sup>1)</sup> H. KAMERLINGH ONNES and C. BRAAK. These Proceedings 9, 367, 1906. Leiden Comm. No. 95e. H. KAMERLINGH ONNES and W. H. KEESOM. These Proceedings 16, 440, 1913. Leiden Comm. No. 137d.

<sup>&</sup>lt;sup>2)</sup> In some cases the indication of the manometer for the innertube was excessively high and irregular, which probably can be ascribed to a partial obstruction of the connecting tube. In these cases  $T_i$  was derived from  $T_e$  by means of the differences  $T_i - T_e$  found with other experiments.

<sup>&</sup>lt;sup>3</sup>) E. Mathias, C. A. Crommelin and H. Kamerlingh Onnes. These Proceedings 23, 1175, 1921, Leiden Comm.  $\mathbb{N}^0$ , 154b.

TABLE I.

1	2	3	4	5	6	7	8	9	10	11	
	2.70		Pre	essure	Temp	erature	Сар	acity	Diele	ctr. cons	st.
Series	Nº.	Date	p <sub>i</sub> cm.	p <sub>e</sub> cm.	$T_i$	T <sub>e</sub>	$C_{H_2}$	$C_V$		corr.	
	1	25 . II	76.8	74.5	20.40	20.29	152.62		1.2309	1.2315	
	2	,,	21.3	20.1	16.73	16.60	154.35		1.2449	1.2455	
	3	**	12.1	10.9	15.47	15.24	154.71		1.2478	1.2484	
I	4	**	8.3	7.0	14.71	14.40	154.81		1.2486	1.2492	
	5	,,			-			123.99			
	7	28 . II	76.9	74.6	20.40	20.30	152.52		1.2301	1.2307	
	12	10 . III	79.0	76.7	20.49	20.39	153.68		1.2299	1.2305	ji
	13	**						124.95			liquid
II	15	12 . III	7.6	6.3	14.56	14.20	156.07		1.2491	1.2497	
	16	"	6.6	5.9	14.29	14.09	156.18		1.2499	1.2505	
	17	**	6.0	5.5 <sup>1</sup> )	14.12	13.99	156.39		1.2516	1.2522	
	19	7 . IV	77.6	75.4	20.43	20.33	115.59			1.2309	
Ш	20	**	51.9	49.7	19.11	19.02	116.03			1.2356	
	21	. "	31.6	30.0	17.73	16.59	116.52			1.2408	
	22	**	5.5	2.9	14.0	13.0	113.24			1.2058	
	25	17. VI		`				85.33			solid
	26	"	4.9	3.0	13.8	13.1	102.23	·	1.1981	1.1986	SC
`	27	**	3.9	2.4	13.5	12.8	102.10		1.1966	1.1971	
IV	28	1. VII						85.34			
	29	••		6.5	(14.69)	14.26	106.73		1.2506	1.2512	)
	30	. 90		5.8	(14.33)	14.07	106.80		1.2515	1.2521	quid
	31	**		5.41)	(14.10)	13.95	106.90		1.2527	1.2533	) =

Dielectric constant of liquid hydrogen at the boilingpoint.

In measurements Nos. 1, 7, 12 and 19 the hydrogen in the cryostat

<sup>1)</sup> Bath solid.

boiled under about atmospheric pressure. By means of the temperature coefficient a=-0.0036 calculated from Nos. 19 and 20, the values of the dielectric constant were reduced to the boilingpoint of hydrogen, T=20.36 <sup>1</sup>). The values, thus obtained, are given in table II under  $\varepsilon_B$ 

TABLE II.

Nº.	. T	., €	Δε	$\varepsilon_B$	Mean value
1	20.40	1.2315	0.0001	1.2316	
7 .	20.40	1.2307	0.0001	1.2308	1.2311
12 .	20.49	1.2305	0.0005	1.2310	± 0.0002 <sub>4</sub>

The measurement  $N^0$ . 19 has not been included, as it was not complete (see p. 41 note 2).

Hence the dielectric constant of liquid hydrogen at 20°.36 K. can be given as

$$\varepsilon_B = 1.2311$$

with a probable error of about 0.02 %.

This result is considerably larger than the provisional value of Breit and Kamerlingh Onnes <sup>2</sup>) ( $\varepsilon=1.21$ ), and differs also somewhat from that of Wolfke and Kamerlingh Onnes <sup>2</sup>) ( $\varepsilon=1.225$ ). Probably the first mentioned difference is due to a too small value being adopted by the observers mentioned for the capacity of the leading wires; we remark that their measurements of the dielectric constant of liquid oxygen gave a value, that was about 1.5 % smaller than provisional measurements performed by us.

The difference between our measurements and those of WOLFKE and KAMERLINGH ONNES, which were made after the same method and partly with the same apparatus, can have the following causes:

- a. the influence of the scale not being uniform increases the value for the dielectric constant by 0.0015 to 0.0021; using other parts of the scale it could be still more;
- b. the correction for the capacity of the supply-cap again increases the result by 0.0006;
- c. Wolfke and Kamerlingh Onnes calculated the temperature from the pressure in the cryostat bath. At the boiling-point of hydrogen the difference with the temperature in the condenser vessel is about  $0.1^{\circ}$ ; by this the dielectric constant is further increased by 0.0004.

From these three circumstances we could increase the value, obtained by the observators mentioned, by 0.003, giving 1.228.

<sup>1)</sup> J. PALACIOS MARTINEZ et H. KAMERLINGH ONNES, 1.c.

<sup>2)</sup> L.c.

d. As Wolfke and Kamerlingh Onnes ascribe to their measurements an accuracy of 0.1 %, we to our measurements an accuracy of 0.02 %, the remaining difference of 0.003, that is of 0.25 %, is explained to about 0.1 %.

TABLE III.

No.	~	Т	ε	ρ	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{\rho}$	
12	С	20.49	1.2305	0.07068	1.0095	
1	a	20.40	2315	7082	0116	
7	ь	20.40	2307	7082	0083	
20	e	19.11	2356	7215	0092	
21	е	17.73	<b>24</b> 08	7360	0096	
2	a	16.73	2455	7 <del>4</del> 57	0145	
3	a	15. <del>4</del> 7	2484	7573	0097	id
4	a	14.71	2 <del>4</del> 92	7641	0038	liquid
29	f	14.69	2512	76 <del>4</del> 3	0109	
15	d	14.56	[ 2497 ]	765 <del>4</del>	[ 0039 ]	
30	f	14.33	2521	7675	0100	
16	d	14.29	[ 2505 ]	7678	[ 0037 ]	
17	đ	14.12	[ 2522 ]	769 <del>4</del>	[ 0079 ]	
31	f	14.10	2533	7695	0118	
22	e	14.0	2059			
26	g	13.8	1987			solid
27	g	13.5	1972			

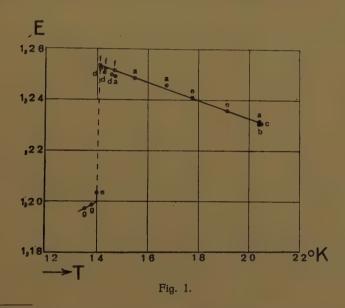
The measurements of the dispersion of liquid hydrogen by AUGUSTIN 1) make it possible to calculate the optical dielectric constant. If we extrapolate the values of AUGUSTIN by means of the simplest dispersion-formula  $n=n_0+a\,\lambda^{-2}$ , we obtain for infinitely long waves  $n_0=1.10921$ , and so  $n_0^2=1.2303$ , at 75.54 cm. Hg., and  $T=20^\circ.30$ . Reduction to  $T=20^\circ.36$  gives  $n_0^2=1.2301$ , a value, which is in satisfactory agreement with our result.

<sup>1)</sup> H. Augustin, Ann. d. Phys. 46, 419, 1915.

# Variation of the dielectric constant of liquid hydrogen with temperature.

Table III gives the results obtained, arranged according to the temperature. Besides the D.  $C. = \varepsilon$  also  $\frac{\varepsilon-1}{\varepsilon+2} \frac{1}{\varrho}$  is given,  $\varrho$  being the density of the substance 1). Fig. 1 represents graphically the course of the D. C. The points obtained on the same measuring day, are indicated by the same character.

The results form almost a straight line. For the deviations, which some points show, we could find a possible explanation  $^2$ ). This is however not the case for  $N^0$ . 2; the deviation of this measurement is 0.0015, and surpasses 3 to 4 times the mean error of the measurement.



<sup>1)</sup> The values taken from MATHIAS, CROMMELIN and KAMERLINGH ONNES (cf. § 5) were extrapolated linearly below 14.8° K.

<sup>&</sup>lt;sup>2)</sup> For  $N^0$ . 4, perhaps also for  $N^0$ . 3, it is possible that the level of the liquid had fallen too much, by which too small values were obtained.

Owing to a displacement of the scale the measurements Nos. 19—22 should not be compared directly with the capacity empty. The indirect calculation based upon the measurement at the boiling-point  $N^0$ . 19, and the D.C. from table II, is somewhat less certain, as this measurement originally meant as control, has been performed somewhat less accurately.

Nos. 15—17 are uncertain, owing to a burst in the condenser detected after those measurements, and because for these measurements the hydrogen was diluted with a little helium. For Nos. 29—31, which, belonging to the same temperature domain show the same temperature course, but gave higher absolute values, the temperature-measurement was uncertain, probably owing to a partial obstruction of the connection tube with the manometer (comp. p. 37 note 2): the error however was probably not more than 0.1° and equal for all these measurements.

Because of this we could say, that a small deviation (of 0.001, measurement  $N^0$ . 2) of the linear course is probable, but not proved.

This course is reproduced in the values of  $\frac{\epsilon-1}{\epsilon+2}\frac{1}{\varrho}$ . But for the measurements Nos. 2 and 4 and the values between [] the function of CLAUSIUS-MOSOTTI is constant to 0.002. The mean value is 1.010. According to Tangl 1) the value is 1.0106 for gaseous hydrogen at 20 atm., 0.9994 at 100 atm.

#### The dielectrical constant of solid hydrogen.

From table I and fig. 1 it appears, that the D. C. of hydrogen decreases abruptly on solidification  $^2$ ).

The results of the measurements Nos. 22 and 26 differ so much from each other, that it is difficult to ascribe that difference only to a change of the D. C. with temperature. We must think here of the spongy structure, forming "vacuols", in the solid hydrogen 3). So the value measured corresponds properly to an ill-defined mixture of solid substance and vapour. For a homogeneous mass it would be somewhat larger. After the mixture-rule of SILBERSTEIN 4) the correction should be  $\Delta \varepsilon = \frac{\Delta v}{v} (\varepsilon - 1)$ ,

 $\frac{\Delta v}{v}$  being the fraction of the total volume occupied by the vapour. According to KAMERLINGH ONNES and CROMMELIN 5) the contraction at the solidification of hydrogen is 4.8 %. In the worst case, that the volume of the vacuols would be equal to the whole contraction, the correction would be 0.0096. This is then the upper limit. Differences in the third decimal of the D. C. are so explained 6).

From measurement  $N^0$ . 22 it follows that the D. C. of solid hydrogen is not below 1.206. We obtained an upper limit, by applying the maximum correction 0.0096 to the value 1.993, which follows from  $N^0$ . 26 by reduction to T=14.0. It is 1.209. So the D. C. of homogeneous solid hydrogen near the meltingpoint lies between 1.206 and 1.209.

It deserves attention that on solidification the polarisation  $P=\frac{\varepsilon-1}{\varepsilon+2}$  decreases from 0.07786 to about 0.0647, thus about 16.8 % where the

<sup>1)</sup> K. TANGL. Ann. d. Phys. 26, 59, 1908.

<sup>2)</sup> The temperature difference between the measurements Nos. 31 and 32 is only 0.1°.

<sup>3)</sup> Remarkable is the small resistance, that the "solid" hydrogen offers on moving the glass tube which surrounds the connecting wire. Also the electric contact in the hydrogen bath is not in the least influenced by the mass solidifying whereas on the contrary it is very sensible for the smallest traces of solid air.

<sup>4)</sup> L. SILBERSTEIN. Ann. d. Phys. 56, 677, 1895.

<sup>&</sup>lt;sup>5)</sup> H. KAMERLINGH ONNES and C. A. CROMMELIN, These Proceedings 16, 245, 1913, Leiden Comm. No. 137a.

 $<sup>^{6}</sup>$ ) We must further remember, that measurement N<sup>0</sup>. 22 underlies the same uncertainty as Nos. 20 and 21 (comp. p. 41 note 2).

density increases by 4.8 %. Hence the function of CLAUSIUS-MOSOTTI decreases at solidification of hydrogen by more than 25 %.

The results of the measurements  $N^{os}$ . 26 and 27 show a small decrease of the D. C. with temperature. The temperatures of these measurements are somewhat uncertain owing to the obstruction in the tube that connects the inner vessel with the manometer. This we took into account in the way mentioned above  $^1$ ). This limits the accuracy of the absolute temperature measurement to  $0.1^{\circ}$  at the utmost.

The course of the curve below the meltingpoint differs from that, obtained in the provisional experiments of Comm.  $N^0$ . 171c. Probably in these measurements, all the hydrogen was not solidified, owing to the slow exchange of the temperature in solid hydrogen.

#### SUMMARY.

- 1. In the method of WOLFKE and KAMERLINGH ONNES for determining the dielectric constant of condensed gases some improvements have been made.
- 2. The D. C. of liquid hydrogen at the boilingpoint (T=20.36) has been measured; from 3 measurements the value  $\varepsilon_B=1.2311\pm0.0002^4$  was obtained.
- 3. The D.C. of liquid hydrogen has been measured at different temperatures from the boilingpoint almost to the meltingpoint. We obtained a linear course. A linear variation was found, although there was an indication of a small deviation. The D.C. near the meltingpoint is 1.2533.
- 4. The D.C. of solid hydrogen has been measured; it is for a homogeneous mass near the meltingpoint 1.206—1.209. On further cooling the D.C. decreases.

<sup>1)</sup> Comp. p. 37 note 2.

Anatomy. — "The cerebellum of fishes. 2. The cerebellum of Megalops cyprinoides (Brouss.) and its connections." By C. J. VAN DER HORST, (Communicated by C. U. ARIËNS KAPPERS.) (Central Institute for Brain Research, Amsterdam.)

(Communicated at the meeting of November 26, 1925).

In Teleosts great variability is found in the shape and the seize of the cerebellum. Dimensions and form of the cerebellum are in close relation to the phylogenetical position of the particular fish and to no less a degree to the habits of the animal. This has been studied by V. Franz in a great number of Teleosts. Also Addison accurately studied and compared the fiber connections of the cerebellum of three Teleosts with different habits, viz. Gadus, Arius and Pleuronectes in the Institute for Brain Research at Amsterdam.

In general the cerebellum is small in fishes that move slowly, like Hippocampus, Pleuronectes, Cyclopterus, Scorpaena and Lophius. On the other hand the cerebellum is large in good swimmers like Clupea, Gadus and Thynnus.

All the different stimuli that reach the central nervous system by way of the sense organs do not have the same influence on the development of the cerebellum. No doubt the most important sense organ for the cerebellum is the lateral line system together with the vestibular organ which is closely related with the former. Direct fibers of the N.N. laterales and the N. octavus end in the cerebellum which also forms an unity with the endnuclei of these nerves in the oblongata. From this as also from the ontogenetic development, it is clear that in the cerebellum originally only ended the octavo-lateralis fibers. It is only later on that secundary and tertiary connections of other centra reach the cerebellum.

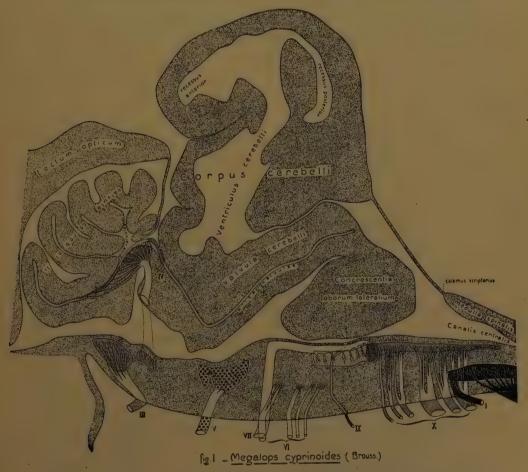
Also very important for the cerebellum is the degree of development of the optic system. The tectum opticum is in direct connection with the cerebellum by the tractus tecto-cerebellaris which is one of the largest afferent tracts of the cerebellum.

Of importance also is the general sensibility of the body. Sensory stimuli can reach the cerebellum by way of the tractus spino-cerebellaris which ascending from the spinal cord and the oblongata ends also in fishes in the cerebellum. The taste and olfactory organs seem to be of small importance. Only by way of tracts of higher order taste and olfactory stimuli may reach the cerebellum probably by means of the tractus lobocerebellaris.

So it is not surprising that the cerebellum of Megalops is very large. As a pelagic fish Megalops is a strong swimmer. The lateral line system is greatly developed and the name of the fish indicates already that it is provided with large eyes. On the contrary the general sensibility of the skin is poorly developed in keeping with the habits of the animal, at least judging from the small seize of the ascending spinal tracts compared with those of Lophius, Trigla etc.

But before discussing the peculiarities shown by this cerebellum in relation with its great development, I should like to call attention to a few particular points that show, that this cerebellum has retained original characters notwithstanding its great development.

At first the ventriculus cerebelli is large (fig. 1). This must be looked



upon as a primitive character, because the cerebellum has a bilateral origin according to Schaper. Whereas in most Teleosts the two halves totally unite, in other more primitive forms among them the lateral halves remain more or less separated by a narrow sagittal, fissurelike ventricle. In the corpus cerebelli of Megalops the right and the left granular masses are

almost entirely separated from each other. A union occurs only in the middle of the dorsal part, by which the ventricle is divided in a recessus anterior and a recessus posterior. To be sure the ventricle in Megalops is also fissurelike, however this fissure is for the greater part strikingly broader than in other Teleosts (fig. 2).

Another primitive character of this cerebellum is the occurrence of a well defined auricle. In a previous communication I tried to make clear, that the auriculus cerebelli is absent in Teleosts or only indicated by a slight accumulation of granular cells. On the contrary the auricle is very clear in Megalops and it is separated from the corpus cerebelli by a deep fissure, comparable with the sulcus para-auricularis described by VOORHOEVE in Selachians. Even a recessus lateralis of the fourth ventricle is present, though this is very small (fig. 3).

Also the ventral part of the granular mass, pushed away by molecular substance in other Teleosts is still a rather compact mass of granules in

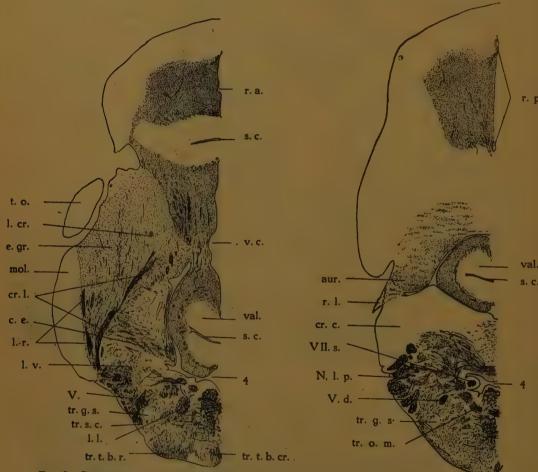


Fig. 2. Crosssection of the frontal part of the corpus cerebelli.

Fig. 3. Crosssection of the caudal part of the corpus cerebelli.

the caudal part of the cerebellum of Megalops. Of course, fibers of the commissura vestibulo-cerebellaris pass through this mass, but in general the granular cells lie densely packed in the whole breadth between the two auricles (fig. 3).

Finally I should like to call attention to the fact that the valvula cerebelli has a simple shape and has no lateral lobes, though it is very large and shows a peculiarity that I have not seen in any other Teleost (fig. 5).

The progressive development of the cerebellum of Megalops is, as we have seen, principally influenced by the lateral line system. Both the N. lateralis anterior and the N. lateralis posterior are very large. It was not possible for me to separate the N. octavus from the N. lateralis anterior with certainty, because the nerves were cut off near the brain surface. In correspondence with the seize of the nerves, the lobus liniae lateralis is very large as is also the crista cerebellaris; the latter is situated at the dorsal side of the lobus. It is not only in the crosssection that they are very large but they also extend in caudal direction farther than I have found in any other bony fish, viz. a little beyond the calamus scriptorius, thus in fact into the spinal cord (fig. 4). The two lobes have fused above

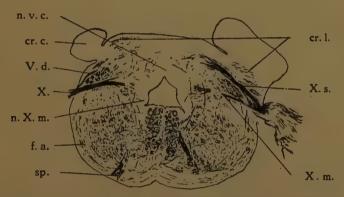


Fig. 4. Crosssection of the spinal cord immediately behind the calamus scriptorius.

the fourth ventricle over a long extend (fig. 1). Such a concrescentia loborum lateralium occurs generally in Teleosts, in which the lateral line system is well developed. A great number of crossing fibers is found here, for the greater part direct lateralis fibers (fig. 3). A very few fibers cross over in the commissura infima (fig. 4). In Anguilla, in which the lateral lobes do not fuse, a great number of lateralis fibers cross over here according to HERRICK.

Near their entrance the two roots split into ascending and descending fibers. It may be that the entering fibers split in two parts. I have not seen it in my crosssections, but I take it for probable, because this dichotomy has been found in other fishes. These fibers intermingle in such a way in the lobe, and also numerous fibers of the lateralis posterior ascend till in front of the lateralis anterior, that it is not possible to

distinguish a lobus anterior and a lobus posterior as BERKELBACH VAN DER SPRENKEL was able to do in Silurus.

But not all lateralis fibers end in the lobe. A great number of them ascends to the cerebellum to spread in the eminentia granularis which, as I have shown before, is in close relation with the lobus liniae lateralis. Among these are also numerous fibers of the lateralis posterior. ADDISON stated, that only fibers of the lateralis anterior reach the cerebellum in Gadus. These fibers end in the eminentia of the same side or they unite to a compact bundle that crosses over in the cerebellum and ends in the eminentia of the other side (fig. 2). Tello found this decussation in the velum; in Megalops it is found in the middle of the cerebellum.

These crossing fibers do not end in the valvula in Megalops; in Gadus they do according to ADDISON.

The eminentiae granulares are very large, but only present in the frontal part of the cerebellum. The caudal part consists only of the corpus cerebelli proper. So in Megalops the eminentiae are stretched out in dorsoventral direction, as this is in fact the case with the whole corpus cerebelli.

The two eminentiae granulares are connected with each other by a great number of commissural fibers that, united in a compact bundle, cross over in the frontal part of the concrescentia loborum lateralium (fig. 2). I take this commissure to be homologous with the commissura interauricularis of WALLENBERG, which has been described by KAPPERS as a small commissure in Gadus but as a very large one in Arius. But there is a striking difference. In Arius this commissure is situated near the peripheral surface of the brain, the decussation is quite ventral. It also curves in a frontal direction. In Megalops on the contrary the fibers take a shorter way. They leave the eminentia at its medial side and run from there directly to the median plane curving only in a caudal direction.

As I have given evidence in a previous communication, the Teleosts in general have no auricle. The commissure, mentioned above, in fact does not connect the two auricles, but the eminentiae granulares; so I think it better to call it the commissura eminentiae granularis. There could be discerned a ventral commissure, as found especially in Arius, and a dorsal one like Megalops has. I think it probable, that the tractus or commissura trigemino-cerebellaris, found by V. Franz very well developed in Silurus, and also the decussating bundle that has been described by Mayser in Cyprinidae as Pons Varoli, are both the same as the commissura eminentiae granularis.

It is selfevident, that also the lateral lemniscus, which, ascending from the oblongata, conducts the octavo-lateral stimuli, is well developed and, in correspondence to this, also its endnucleus, the torus semicircularis, is very large (fig. 6). But these are not the only fibers that end in the torus semicircularis. At first fibers of the N. opticus enter the torus along its whole length and end in the ventral part of the torus (figs. 5 and 6). I have never found these direct opticus-fibers in any other fish.

Secundly also of the secundary fibers that leave the tectum opticum some pass through the torus with which they are probably connected. These secundary fibers are arranged in three superposed systems (figs. 5 and 6). The most ventrally situated fibers form the tractus tecto-bulbaris cruciatus, which curving around the dorsal side of the commissura transversa runs in median direction. The fibers lying in the middle are more diffusely scattered or form small bundles. They unite farther caudally to the very large tr. tecto-bulbaris rectus. The third, most dorsally situated system of fibers runs in the caudal part of the mid-brain through the torus semicircularis and parallel its surface (fig. 6). In the most caudal part these fibers can not be distinguished from those of the tr. tecto-bulbaris rectus, which also makes a dorsally directed curve in the torus. I think it probable, that many of these last mentioned fibers end in the torus or at least have

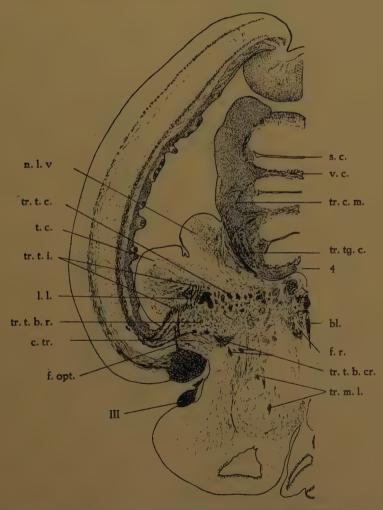


Fig. 5. Crosssection of the middle part of the tectum opticum and of the valvula cerebelli.

connections here. They end in a row of glomerulilike arborisations, which lie at the median border of the torus and caudally to the nucleus lateralis valvulae (fig. 6.) Farther frontally these fibers run directly, without curving through the torus semicircularis, to the glomeruli, piercing through the lemniscus lateralis (fig. 5). I suppose these fibers which come as the most dorsal ones from the tectum opticum to constitute the tr. tecto-isthmicus and then the glomeruli with the surrounding cells are the ganglion isthmi.

It is very difficult to trace the afferent connections of the nucleus lateralis valvulae. I agree with KAPPERS, when he supposes that this nucleus is closely related with the torus semicircularis, so that octavus and lateralis stimuli will reach it. But also it receives optic stimuli from the torus and the ganglion isthmi, also direct fibers from the tectum opticum reach this nucleus. Many fibers from the nucleus lateralis valvulae run along the ventricle at the dorsal side of the fasciculus longitudinalis posterior in a

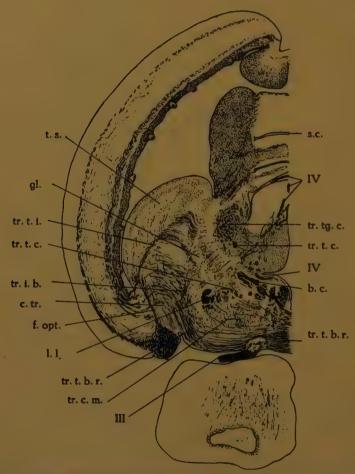


Fig. 6. Crosssection of the caudal part of the tectum opticum and of the valvula cerebelli.

median direction and seem to decussate. I could not state the origin of these fibers, but I suppose that they are crossing fibers from the torus semicircularis, because also many fibers from the torus take the same direction (fig. 5).

The large tractus mesencephalo-cerebellaris posterior or tegmento-cerebellaris runs from the nucleus lateralis valvulae to the cerebellum. At its caudal side follows the tractus mesencephalo-cerebellaris anterior or tecto-cerebellaris. This latter bundle has a different course in Megalops to that usually met with in Teleosts. Generally it leaves the tectum opticum where, at its frontal end, the median part of the tectum fuses with the tegmentum. From here the tract runs as a compact bundle through the tegmentum at the median side of the lemniscus (fig 5), it bends towards the corpus cerebelli just behind the tractus mesencephalo-cerebellaris posterior and runs here near the midline to its endings in the caudal part of the corpus. The number of fibers leaving the tectum at its frontal end near the midplane is very small in Megalops. These fibers are joined by numerous other ones that, arising in the frontal part of the tectum, reach the tegmentum by way of the lateral attachment of the tectum and, arranged in small bundles, they run in a caudal direction.

These fibers leave the tectum in the same way as, on a more caudal level, the fibers that run to the ganglion isthmi do (fig. 5). Also in the cerebellum these fibers have not the course otherwise met with, but are situated quite laterally in connection with the tractus tegmento-cerebellaris.

Whereas the tractus tecto-cerebellaris spreads wholly in the corpus cerebelli, the tractus tegmento-cerebellaris sends the greater part of its fibers to the valvula. This bundle is a very large one in Megalops. In correspondence with this the valvula is also very large. As said before the valvula has a comparatively simple form, but only in that the lateral lobes are absent (fig. 5). But the rather narrow midpart is very long and lies in many curves under the roof of the midbrain. A simple shaped valvula makes only one curve in general, sometimes a secundary curve can be added like in Gadus and Perca. I found in Megalops no less than six secundary curves.

A striking peculiarity of the valvula of Megalops is, that it is not only situated below the tectum opticum, but it stretches also caudally in the fourth ventricle like a fingershaped organ untill near the caudal side of the corpus cerebelli (figs. 1, 2 and 3). This part has the typical structure of a valvula with the granular layer at the outside and the molecular layer, in which extends the skullcavity, at the innerside. It is situated in the ventricle quite free, but for a possible superficial fusion with the concrescentia loborum lateralium. I found this fusion in one series but not in the other. No fibers enter the valvula from the concrescentia.

The other afferent systems are slightly developed. The tractus spinocerebellaris and olivo-cerebellaris are very thin and have the normal course for these tracts (fig. 2). The tractus lobo-cerebellaris is not present as a well

defined bundle. Numerous isolated fibers join the tractus tecto-cerebellaris, where this enters the cerebellum. These fibers come from the ventral part of the bulbus to which part run also fibers from the lobi inferiores.

The tractus cerebello-motorius leaves the cerebellum along the mediocaudal side of the very small gustatory nucleus. The more medially situated fibers, which originate all in the corpus cerebelli, form a compact bundle that, piercing through the fasciculus longitudinalis posterior, decussates just behind the oculomotor nucleus (fig. 6).

Also the more laterally situated fibers decussate at this level. So the decussation is not drawn out in Megalops as FRANZ found it in other Teleosts, but it is limited to a small area. The lateral fibers, which run to the midline more in a curve, arise principally in the valvula; they form a great number of small bundles which partly pierce through the tractus tecto-cerebellaris.

Megalops is one of the most primitive Teleosts. In correspondence to this the cerebellum shows several primitive characteristics and to a greater number and more primitive than the simple cerebellum of Osmerus, and even, as to the auricle, than that of Amia. On the other hand the cerebellum is greatly developed in connection with the habits, whereby especially the valvula shows particular peculiarities.

#### LITERATURE.

- W. H. F. ADDISON. A comparison of the cerebellar tracts in three teleosts. Jour. Comp. Neur., Vol. 36. 1923.
- C. U. ARIENS KAPPERS. Die vergleichende Anatomie des Nervensystems der Wirbeltiere und des Menschen. II Abschnitt. Haarlem. 1921.
- H. BERKELBACH VAN DER SPRENKEL. The cranial nerves of Silurus glanis and Mormyrus cashive. Jour. Comp. Neur., Vol. 25. 1915.
  - V. FRANZ. Das Kleinhirn der Knochenfische. Zool. Jahrb. Abt. Anat., Bd. 32. 1911.
- C. J. VAN DER HORST. The cerebellum of fishes. I. General morphology of the cerebellum. Proc. Kon. Ak. Wet. Amsterdam, Vol. 34, 1925.
- P. MAYSER. Vergleichend anatomische Studien über das Gehirn der Knochenfische mit besonderer Berücksichtigung der Cyprinoiden. Zeitschr. Wiss. Zool., Bd. 36.
- A. SCHAPER. Die morphologische und histologische Entwicklung des Kleinhirns der Teleostier. Anat. Anz. Bd. 9. 1894.
- F. TELLO. Contribución al conocimiento del encéfalo de los teleósteos. I. Los nucleós bulbares. Trabajos del laboratorio de investigaciones biologicas. Madrid. Tomo 7, 1909.
- N. VOORHOEVE. Over den bouw van de kleine hersenen der Plagiostomen. Diss. Amsterdam. 1917.

#### LIST OF ABREVIATIONS

aur.	auriculus cerebelli.	cr. c.	crista cerebellaris.
b. c.		cr. 1.	primary lateralis fibers before the
bl	blood vessel.		
	commissura eminentiae.		

e. gr.	eminentia granularis.	t. o.	tectum opticum.
f.a.	fibrae arcuatae.	tr.c.m.	tractus cerebello-motorius.
f. opt.	fibers of the Nervus opticus.	tr. g. s.	tractus gustatorius secundarius.
f. r.	fasciculus retroflexus.	tr. i. b.	tractus isthmo-bulbaris.
gl.	glomeruli.	tr. m. l.	tractus mesencephalo-lobaris.
1. cr.	primary lateralis fibers after the	tr. o. m.	tractus octavo-motorius.
	decussation.	tr. s. c.	tractus spino-cerebellaris.
1. 1.	lemniscus lateralis.	tr. t. b. cr.	tractus tecto-bulbaris cruciatus.
1. r.	non crossing lateralis fibers.	tr. t. b. r.	tractus tecto-bulbaris rectus.
1. v.	lobus liniae lateralis ventralis.	tr. t. c.	tractus tecto-cerebellaris.
mol.	molecular mass.	tr. tg. c.	tractus tegmento-cerebellaris.
N. l. p.	Nervus lateralis posterior.	tr. t. i.	tractus tecto-isthmicus.
n. l. v.	nucleus lateralis valvulae.	t. s.	torus semicircularis.
n. v. c.	nucleus visceralis commissuralis.	val.	valvula cerebelli.
n. X. m.	nucleus vagi motorius.	v. c.	ventriculus cerebelli.
r. a.	recessus anterior of the ventri-	III.	Nervus oculomotorius.
	culus cerebelli.	IV.	Nervus trochlearis
r. l.	recessus lateralis of the fourth	V.	Nervus trigeminus.
	ventricle.	V. d.	trigeminus descendens.
r. p.	recessus posterior of the ventri-	VII. s.	Nervus facialis sensibilis.
	culus cerebelli.	X.	Nervus vagus.
s. c.	skull cavity.	X. m.	motor vagus root.
sp.	Nervus spinalis.	X. s.	sensory vagus root.
t. c.	torus semicircularis.	4.	fourth ventricle.

Chemistry. — "On the Crystalforms of some position-isomeric Dinitroto-luenes". By Prof. F. M. JAEGER.

(Communicated at the meeting of October 31, 1925).

§ 1. In the following article are communicated the results of the crystallographic measurements made with a number of position-isomeric Dinitrotoluenes, which had been were prepared by Dr. H. A. SIRKS 1) and given to me by this author for the purpose mentioned. It appeared possible to obtain five of the six possible isomerides in a form suitable for measurement. For the purpose of comparison also some measurements are considered here, made with some other nitro-derivatives of toluene by BODEWIG 2), CALDERON 2) and FRIEDLÄNDER 3).

§ 2. 1-2-3-Dinitrotoluene :  $C_6H_3(NO_2)_2$ ; Mpt. 60° C.

This substance was obtained from ether in the shape of small, almost colourless tabular crystals. They are well built and show constant angular values.

Rhombic-bipyramidal.

$$a:b:c=0.6352:1:0.3721.$$

Fig.1.

Forms observed:  $c = \{001\}$ , predominant, very lustrous;  $m = \{110\}$ , well developed and yielding very sharp images;  $r = \{101\}$ , large and well reflecting;  $o = \{111\}$ , extremely narrow, mostly absent, and yielding only faint reflections. The habit of the crystals is tabular parallel to  $\{001\}$ .

Angular values:	Obse	erved:	· Cai	lculated
$c: r = (001): (101) =^*$	30°	211/2	-	-
$m: m = (110): (1\overline{10}) =^*$	64	51	-	-
m: c = (110): (001) =	90	0	90°	0′
$m: m = (110): \overline{(1}10) =$	115	9	115	9
$r: r = (101): (10\overline{1}) =$	119	25	119	7
m:o = (110):(111) =	36	391	36	58
o: c = (111): (001) =	53	201	53	2 <del>1</del>

No distinct cleavability was found.

<sup>1)</sup> H. A. SIRKS, Dissertatie, Groningen, (1906).

<sup>&</sup>lt;sup>2</sup>) C. BODEWIG, Zeits. f. Kryst., 3, 388, (1879); L. CALDERON, ibid., 4, 235, (188

<sup>&</sup>lt;sup>3</sup>) P. FRIEDLÄNDER, Zeits. f. Kryst., 3, 170, 173, (1879).

#### § 3. 1-2-4-Dinitrotoluene; Mpt.: 71° C.

From a mixture of ether and alcool this compound was obtained in colourless, flat needles.

#### Monoclinic-prismatic.

$$a:b:c=0.8553:1:0.5236;$$
  
 $\beta=84^{\circ}37\frac{1}{2}'.$ 

Forms observed:  $m = \{110\}$  and  $b = \{010\}$ , large and very lustrous;  $a = \{100\}$ , much narrower than either of these forms, but yielding good reflections;  $r = \{101\}$ , large, but dull;  $c = \{001\}$ , small and yielding only faint images;  $o = \{111\}$ , narrow, but very lustrous;

 $p = \{120\}$ , extremely narrow. The shape of the crystals is prismatic parallel to the *c*-axis.

					/		1/3	
Angular Values:	Measu	red:	Calcu	lated :				
m: r = (110):	(101) =* 63°	52½′	. <del>-</del>	_				
m:b=(110):	(010) = * 49	35	-	-				
r:o = (101):	(111)=* 39	48	-	-	b'		6	
m:o=(110):	(111) = 76	19 <del>1</del> ·	76°	$19\frac{1}{2}'$		m		
a:r=(100):	(101) = 54	38	54	40	m	1 1	1	
a: m = (100):	(110) = 40	25	40.	25		1-1	N	
p:b=(120):	(010) = 29	491	30	25				
p:n=(120):	(110) = 19	26	. 19	10		r		
c:r=(001):	(101) = 29	471	29	57½	/	الرا	,	
a:c = (100):	(001) = 84	25	84	371	7	) '		
c:b=(001):	, ,	0	90	. 0		Zi 0		
o:b=(111):	(010) = 62	<b>35</b> /	62	28	F	ig.2.		

No distinct cleavage could be observed.

The optical axial plane is perpendicular to {010}.

This substance was also studied by BODEWIG <sup>1</sup>); with his (pale yellow) crystals this author found: a:b:c=0.8593:1:0.5407;  $\beta=85^{\circ}$  12'. Perhaps small traces of impurities are responsible for the differences of angular values compared with those here observed.

#### § 4. 1-2-6-Dinitro-toluene; Mpt. 66° C.

From ethylacetate this isomeride was obtained as big, flat, and colourless crystals, showing constant angular values and permitting accurate measurements <sup>2</sup>).

<sup>1)</sup> C. BODEWIG, loco cit., p. 389.

<sup>2)</sup> See also: K. HEYDRICH, Zeits. f. Kryst., 48, 268, (1911). The melting-point mentioned there is 6° too low.

## Rhombic-bipyramidal (pseudohexagonal).

a:b:c=0.5725:1:0.5324.

Forms observed:  $m = \{110\}$ , broad highly lustrous;  $b = \{010\}$ , also well developed and yielding good reflections;  $r = \{101\}$ , narrow, but eminently reflecting;  $q = \{011\}$ , also strongly lustrous: s = 012, narrow, yielding sharp images.

Angular values:	Measur	ed:	Calcui	lated :		1	7	
m: m = (110): (1	10) =* 59°	59′	-	-	m	m		
b:q=(010):(0	011)=* 61	58		_		""		1
b: m = (010): (1	10) = 60	12 <del>1</del>	60°	$12\frac{1}{2}'$				
q:s=(011):(0	(12) = 13	6	13	7 <del>1</del>				
s:c=(012):(0	(01) = 14	57	14	5 <del>4</del> 1			1.5	
m:q=(110):(0	(11) = 76	23½	76	29½	2	SCA	9	

Cleavage distinct parallel to {001}.

The shape of the crystals is elongated parallel to the Fig.3. c-axis, either parallel to  $\{010\}$ , or to a pair of faces of  $\{110\}$ . Sometimes hexagonally limited plates were obtained, showing only  $\{001\}$ , with m and b as bordering facets. The plane of the optical axes is  $\{100\}$ , with c-axis as first bissectrix.

### § 5. 1-3-4-Dinitro-toluene; Mpt. 60° C.

From a mixture of benzene and ethyl-alcool the substance crystallizes in very thin, transparent needles, which mostly show no limiting faces at the top, beyond the basis  $\{001\}$ . Rarely, however, a form  $q = \{011\}$  was observed, only very small.



Fig.4.

#### Monoclinic-prismatic.

$$a:b:c=0.8320:1:0.2465;$$
  
 $\beta=88^{\circ}25'.$ 

Forms observed:  $a = \{100\}$ ,  $m = \{110\}$  and  $p = \{120\}$ , all three about equally broad and yielding good images;  $b = \{010\}$ , somewhat narrower  $c = \{001\}$ , well reflecting;  $q = \{011\}$ , small and giving only faint reflections. The crystal-habitus is elongated parallel to the c-axis.

Angular values:	Observed	: Calculated:
m:b=(110):(010)	)=* 50° 1	5' —
$q:p=(011):(\overline{1}20$	)=* 79	3
q:c=(011):(001)	)=* 13- 5	0 <del>1</del>

Angular Values: Observed: Calculated: 
$$c: p = (001): (120) = 89^{\circ} 8\frac{1}{2}'$$
 89° 11'
 $a: c = (100): (001) = 88$  27 88 25
 $c: b = (001): (010) = 90$  0 90 0
 $a: m = (100): (110) = 39$  45 39 45
 $m: p = (110): (120) = 19$  18 19 14\frac{1}{2}

No distinct cleavage could be observed.

The extinction on m, p and b differs only inappreciably from 90°.

§ 6. It may be remarked in connection with the measurements of the isomeric 1-2-4- and 1-3-4-Dinitrotoluenes, which both are derivatives of p-Nitrotoluene, that this last (Mpt. :  $54^{\circ}$  C.), is rhombic-bipyramidal, with: a:b:c=0.9107:1:1.0965 and the forms:  $\{110\}$ ,  $\{011\}$ ,  $\{211\}$ ,  $\{001\}$ , and  $\{010\}$ . The crystals are perfectly cleavable parallel to  $\{010\}$ . The plane of the optical axes is parallel to  $\{100\}$ , with the c-axis as first bissectrix of negative character. The dispersion is:  $\varrho > v$ .

Furthermore measurements are made of: 1-2-4-6 and 1-3-4-6-Trinitro-toluene; both these compounds are also rhombic-bipyramidal, 1-2-4-6-trinitrotoluene (Mpt.: 82° C.) has the parameters: a:b:c=0.7586:1:0.5970, and exhibits the forms: {110}, {010}, {210} and {011}. The optical axial plane is {001}, the double refraction is negative. 1-3-4-6-Trinitrotoluene (Mpt.: 104° C.) possesses the axial ratio: a:b:c=0.9373:1:0.6724, and shows the forms: {010}, {111}, {120}, {021} and {001}. This compound has a positive double refraction; the plane of the optical axes is {100}.

From these data it is clear that there does not exist a close form-analogy between the mono-, di- and tri-nitro-derivatives of toluene; at the utmost, one might speak of some relation in the value b:c in the 1-2-4-derivative and in p-Nitrotoluene, if for the c-axis half the measured value be taken, while the angle  $\beta$  decreases from 90° to 84°  $37\frac{1}{2}$ ′ Then also a certain analogy can be seen in the relations b:c of these two compounds with the 1-2-6- and 1-3-5-derivative (see below), although, as a fact these isomerides cannot be considered to be derivatives of p-Nitrotoluene. As a final result, therefore, it must be considered to be artificial to indicate any crystallographical relationship here, — the more so, as the 1-3-4-derivative on the other hand does not show any relation of this kind with respect to the substances mentioned in the above.

#### § 7. 1-3-5-Dinitro-toluene; Mpt.: 93° C.

From a mixture of benzene and carbodisulphide, peculiarly shaped individuals were obtained, being wedge-shaped. They appeared, however, completely identical with the monoclinic crystals, obtained by BARNER <sup>1</sup>) from a mixture of benzene and acetic acid. They are bordered by {001}, two planes of {110} and two planes of {111}, i. e. {111} and {111}, and

<sup>1)</sup> F. BARNER, Zeits. f. Kryt., 9, 300 (Ref.).

also by a number of strongly curved faces, giving the shape of a lance-point to the crystals dealt with here (Fig. 5).

Monoclinic-prismatic (pseudo-rhombic).

$$a:b:c=0.4691:1:0.5276;$$
  
 $\beta=89^{\circ}51'.$ 

Forms observed: o' =  $\{11\overline{1}\}$ , rather large and well reflecting;  $m = \{110\}$ , narrower than o', also lustrous;  $c = \{001\}$ , large, is striated parallel to the edge (001): (010).

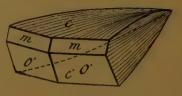


Fig.5.

The indices of the curved faces were not determinable.

Angular Values:	C	bserv	red:	BAR	NER:	Calo	culated.
c: m = (001): (110)	0)=*	89°	50′	89°	50'	-	-
$m: m = (110): (1\overline{10})$	0) ==*	50	12	50	15 <del>1</del>	-	-
$m: o' = (110): (11\overline{1})$	Ī)=*	38	51	38	53	-	_
$o':o'=(11\overline{1}):(1\overline{1})$	<u>1</u> )=	38	41	· <b>38</b>	41	38°	41'
$c:o'=(00\overline{1}):(11\overline{1})$	ī)=	51	18	51	15	51	22

m m

Fig.6.

No distinct cleavability present.

The plane of the optical axes is perpendicular to  $\{010\}$ ; on m the extinction is almost normally orientated. If this compound is recrystallized from ethyl-acetate, beautiful transparent crystals of the shape of Fig. 6 are obtained, which, however, soon become dull and opaque.

Monoclinic-prismatic,  

$$a:b:c=0.7143:1:0.3853;$$
  
 $\beta=73^{\circ}58\frac{1}{4}',$ 

Forms observed:  $m = \{110\}$  and  $r = \{101\}$ , large and highly lustrous;  $s = \{\overline{101}\}$ , somewhat narrower than r, but well reflecting;  $b = \{010\}$ , rather narrow, but yielding very sharp reflections. The habitus of the crystals is short-prismatic along the c-axis.

Angular Values:	Observed:	Calculated :
$m: m = (110): (1\overline{10}):$	=* 68° 65½'	
m:r:=(110):(101):	=* 57 46	
$r: s = (101) : \overline{(101)}$	<del>=</del> * 55 38	
m:b = (110):(010):	= 55 32	55° 32′

No distinct cleavage was found.

Evidently no direct morphotropic relations exist between these crystals and those of the pure substance.

Groningen, Laboratory for Inorganic Physical Chemistry of the University.

Chemistry. — "On Complex Cobaltic Salts with nine-valent Ions"
By Prof. F. M. JAEGER and P. KOETS.

(Communicated at the meeting of December 19, 1925).

§ 1. If a trivalent pseudo-base B reacts with complex cobaltic salts of the type:  $Co\binom{(E\"{i}ne)_2}{X_2}$  Y, where X is a negative substituent and Y a

monovalent ion, or with those of the type:  $Co \begin{pmatrix} (Eine)_2 \\ X \\ Z \end{pmatrix} Y_2$ , where Z is

an indifferent group 1), the possibility occurs of getting salts of a new kind of complex ion of the type:

$$\left\langle (E\"{i}ne)Co:B:Co(E\"{i}ne)_{2}\right\rangle ^{IX} \text{, or } \left\langle \begin{bmatrix} B\\ \vdots\\ Co(E\"{i}ne)_{2}\end{bmatrix}_{3}\right\rangle ^{IX},$$

the new complex ion being now nine-valent. It is, of course, necessary in this case, that the pseudo-base B contains three completely equivalent  $NH_2$ -groups; as  $X_2$  or XZ can only be substituted by two groups  $NH_2$ , two molecules of B will then link together three of the original cobaltic complexes. According to some experiments of POPE and MANN 2), Triaminotriethylamine:  $N(CH_2-CH_2-NH_2)_3$ , although possessing a tertiary N-atom of only feebly basic properties, would occupy four coordinative positions in complex salts; a fact, which they proved i.a. by the preparation of some salts of bivalent nickel and platinum of the type:  $\{Ni(Triam)\}(SCN)_2$ , and  $\{Pt(Triam)\}I_2$ , in which the central metal-atom has the coordination-number four. However, in consideration of the fact, that the N-atoms of the three  $NH_{2}$ -groups of this base exhibit another chemical function than the fourth N-atom, one can foresee the possibility, that the base mentioned might, in the case supposed in the above, eventually react also as a trivalent one with respect to its coordinative functions.

It appeared, that triamino-triethylamine in aqueous solution, reacting with diethylenediamine-dichloro-cobaltic-chloride or with diethylenediamine-chloro-aquo-cobaltic-chloride or -sulphate, gave indeed salts of one of the types mentioned in the above. These compounds are of interest, as well by the very high valency of their complex ions, as by the fact

<sup>1)</sup> Eine is used in these formulae, as in most cases, as an abbreviation for ethylene-diamine: NH<sub>2</sub>. CH<sub>2</sub>. CH<sub>2</sub>. NH<sub>2</sub>; in the same way Triam as an abbreviation for triamino-triethylamine.

2) F. G. MANN and W. J. POPE, Chemistry and Industry Review, 44, 834, (1925).

that an uneven number of the original, - in the case of the cis-configurations at least possibly resolvable complex ions, - are linked together. Indeed, salts of the type:  $\left\{Co\frac{(E\"{i}ne)_2}{X_{\parallel}}\right\}Y$  are, if they have a cis-configuration, resolvable into enantiomorphous isomerides, even when both substituents X are identical; the linking together of an uneven number of such enantiomorphous complex ions must, therefore, - because they are present in equal numbers in the optically inactive solution, - lead to a number of combinations, which at least will correspond to three different kinds of isomerides. For if the supposition is made that in triaminotriethylamine the three radicles: (-CH2. CH2. NH2) and the fourth N-atom are situated in the same plane, and that this situation persists also in the complex ions, then, in the case of the cis-configuration, three isomerides will be possible (Fig. 1), of which two (1<sup>a</sup> and 1<sup>b</sup>) possess only a single axis of binary symmetry, while the third (3°) is completely asymmetrical. As these three isomerides possess merely axial symmetry, they must, therefore, be resolvable into enantiomorphous forms, and yield six kinds of optically active molecules.

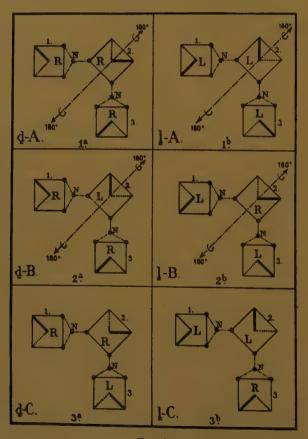


Fig. 1.

If, however, only two of the groups:  $(-CH_2.CH_2.NH_2)$  are situated in the same plane with the fourth N-atom, — the third radicle being situated outside of that plane, — then six isomerides (cis- and trans-forms) are possible (Fig. 2), which all six will be resolvable into optical antipodes.

For in this case each of the thus generated threefold complexes will

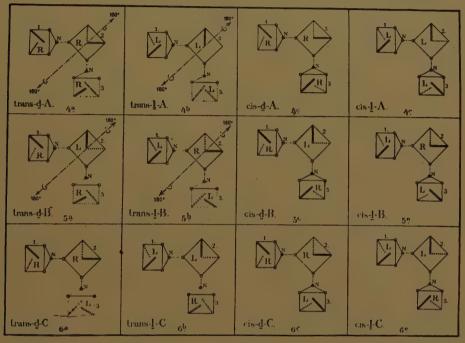


Fig. 2.

possess a spatial configuration differing from its mirror-image; each of these threefold ions, therefore, will represent a racemic compound, which may be resolved into optically active forms. Up till now, however, it was only possible to separate a single homogeneous compound from the reaction-mixture, which opposed to all tentatives of resolving it by means of optically active acids. In this connection it may be remarked, that a threefold complex ion of the second type proposed in the above, can under no circumstances whatsoever be resolved into enantiomorphous forms. In the following also those tentatives will be reviewed, which were made with the purpose of resolving the optically inactive salts obtained.

§ 2. The salts:  $\left\{C_0 \frac{(E\ddot{i}ne)_2}{Cl_2}\right\} Cl$  (green) and  $\left\{C_0 \frac{(E\ddot{i}ne)_2}{Cl}\right\} Cl_2$  (violet), from which we started in this investigation, were prepared after the

methods described in literature. The green praseo-salt is rapidly changed into the isomeric cis-compound when heated in solution; the complex salts of the type here considered, appeared, moreover, to be identical, if prepared by the action of the base either on the green praseo- or on the violet chloro-aquo-salt. Yet, as we shall see afterwards, the complex salt generated must in reality be a derivative of the isomeric ions in trans-configuration.

The triaminotriethylamine used in these experiments was prepared after the method published by RISTENPART 1), but varied with respect to its particularities. The original compound used in this synthesis is  $\beta$ -bromo-

which at a temperature not exceeding 150° C triphtalyl-triamino-triethylamine:  $\begin{pmatrix} C_6H_4 & CO \\ CO & N \end{pmatrix}$  .  $CH_2$  .  $CH_2$   $CH_3$   $CH_4$   $CH_4$   $CH_4$   $CH_4$   $CH_5$   $CH_6$   $CH_6$  CH

introducing dry ammonia into the molten mass. This compound is then afterwards split by means of concentrated hydrochloric acid, yielding the desired base in form of its hydrochloride. Now it soon became evident, that the reaction with gaseous ammonia led to the final state only very slowly. We tried, therefore, to get a better yield by prolongation of the time of reaction. The temperature cannot appreciably be elevated, brown decomposition-products being formed as soon as 150° C. is surpassed; these accessory products highly impede the ready crystallisation of the desired compound. It appeared, that after introducing the gaseous  $NH_3$  during 4 hours, a yield of the base of  $27\,^0/_0$  was obtained; during 8 hours: of  $45\,^0/_0$ ; and during 10 hours: of  $65\,^0/_0$  of the weight of the  $\beta$ -bromoethylphtalic-imide originally used. A further increase of the time of reaction did not increase the yield of the final product to any appreciable extent. The unchanged  $\beta$ -bromoethyl-phtalic-imide is afterwards separated from the reaction-mass and purified for further use.

In most experiments a slow current of dry  $NH_3$ -gas was during 10 hours introduced into 125 grams of molten  $\beta$ -bromo-ethyl-phtalic-imide, which was put into a round-bottom vessel, which was heated in a bath of graphite at  $140^{\circ}-150^{\circ}$  C. After a short time the content of the vessel becomes viscous, while  $NH_4Br$  is separated out, crystallizing partially in the neck of the flask. The reaction being finished, the yet warm product is extracted three times with 80 ccm boiling alcohol of  $97^{\circ}/_{\circ}$ ; the residue is firmly pressed between filter-paper and recrystallised from boiling acetic acid. The recrystallised product melts at  $187^{\circ}$  C. From the alcoholic

<sup>1)</sup> E. RISTENPART, Ber. d. d. chem. Ges., 29, 2531, (1896).

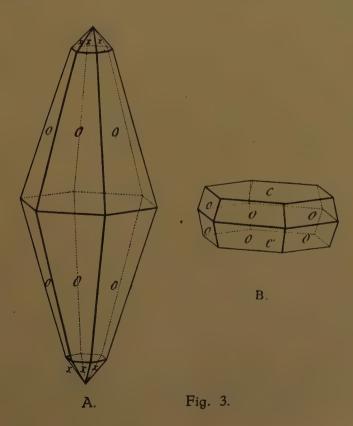
<sup>&</sup>lt;sup>2</sup>) S. Gabriel, Ber. d. d. chem. Ges., 21, 566, (1888); 22, 1137, (1889). This compound was prepared by heating 100 grams of the potassium-salt of phtalic-imide with 399 grams of ethylene-bromide during seven hours, and by eliminating the simultaneously formed ethylene-diphtalic-imide from the reaction-mixture.

filtrate about 20 grams of  $\beta$ -bromo-ethyl-phtalic-imide, after evaporating to dryness and extracting the solid residu with carbondisulphide, can be separated. The yield of pure *triphtalyl-triamino-triethylamine* was 75 grams, besides a small amount of its hydrochloride.

The compound thus obtained is inclosed into glass tubes, each containing 25 grams of it and 60 ccm strong hydrochloric acid (sp. gr.: 1,19); the sealed glass-tubes are heated during two hours at 150° C. in a CARIUS-furnace. After cooling, the tubes, on opening, show in most cases only a small over-pressure; their content is diluted with water, the phtalic acid is filtered off, and the filtrate evaporated. The strongly concentrated solution is afterwards mixed with alcohol + ether; the hydrochloride of triaminotriethylamine is in this way soon precipitated in a good crystalline form. The yield of hydrochloride is about 93  $^{0}$ / $^{0}$ 0 of the calculated quantity.

On slow evaporation of an aqueous solution of the hydrochloride, steep bipyramidal crystals were obtained; analysis gave: 41,73  $^{0}/_{0}$  Cl and 21,69  $^{0}/_{0}$  N; calculated for  $N(CH_{2}.CH_{2}.NH_{2})_{3}$ , 3HCl: 41,59  $^{0}/_{0}$  Cl and 21,92  $^{0}/_{0}$  N.

Crystal-form of Triamino-triethylamine-hydrochloride:  $N(CH_2, CH_2, NH_2, HCl)_3$ .



From the acid solution in water the compound crystallizes in steep, colourless, often spindle-shaped crystals or hexagonal tables.

Hexagonal-bipyramidal. 
$$a: c=1:3,2914.$$

Forms observed:  $0 = \{10\overline{11}\}$ , highly lustrous and yielding excellent reflection-images;  $x = \{10\overline{13}\}$ , usually absent, always very small and giving dull reflexes. The crystals are well built, but some planes of 0 often show laddershaped projections, as a result of a repeated growth parallel to {0001}. The angular values in the zone 0:c are, therefore, often inconstant.

Angles: Observed: Calculated: 
$$0:0=(10\overline{1}\,1):(01\overline{1}\,1)=57^{\circ}\,50'$$
 —  $0:0=(10\overline{1}\,1):(10\overline{1}\,1)=29^{\circ}\,18'-29^{\circ}\,50'\,29^{\circ}\,29'$   $0:x=(10\overline{1}\,1):(10\overline{1}\,3)=21^{\circ}\,15'$  21° 24'

The optical extinction on  $\theta$  is perpendicular and parallel to the edge  $\theta$ : c. Cleavage evidently occurs along {0001}.

In convergent light the interference-image of an uniaxial crystal is observed, exhibiting no circular polarisation. The double refraction is rather strong and of negative character.

The free base cannot be obtained from the hydrochloride by distilling the solution, after addition of potassiumhydroxide in excess, with steam, the base not being appreciably volatile with water-vapour. The finely powdered salt, mixed with an excess of also finely powdered potassiumhydroxide was, therefore, distilled directly from a silver flask. The pure base boils under ordinary pressure at 265° C.; it is a colourless liquid, which under reduced pressure (15 m.M.) distils at 114° C. From 100 grams of  $\beta$ -bromo-ethyl-phtalic-imide ordinarily about 6 grams of the pure, anhydrous base were obtained. The preparation of the complex salts took place by means of solutions, containing  $8-11^{\circ}$  of the base.

§ 3. The preparation of the complex Cobaltic-salts.

4.8 Grams of 
$$Co$$
  $Cl$   $Cl_2$ , solved in 50 ccm. water, were during

4 hours heated on the waterbath with 1,53 grams triaminotriethylamine in  $8.76^{\circ}/_{\circ}$  aqueous solution. After evaporating, from the filtered solution finally a chloride was obtained, possessing a slightly more reddish colour than the luteo-salts and having the composition:

$$Co_3 \frac{(Eine)_6}{(Triam)_2} Cl_9 + 6H_2O$$
, as was proved by analysis.

Analysis:  $8,10^{\circ}/_{0}$   $H_{2}O$ ;  $13,75^{\circ}/_{0}$  Co;  $25,61^{\circ}/_{0}$  Cl;  $21,6^{\circ}/_{0}$  N. Calculated for the composition mentioned above: 8,6%, H2O; 14,01%, Co; 25,34%, Cl; 22,3 %. In the anhydrous salt were found: 14,92% Co; 27,68% Cl and 24,34 % N; calculated 15,40 % Co; 27,83 % Cl and 24,4 % N.

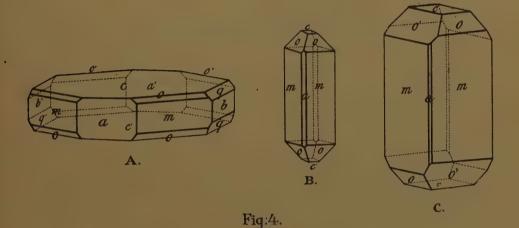
If a strong solution of NaI, be added to a concentrated solution of the *chloride*, a pretty orange-coloured *iodide* is precipitated, which after filtering, washing with water, alcool and ether, appeared to be anhydrous;

it has the composition:  $\left| Co_3 \frac{(E\"{i}ne)_6}{(Triam)_2} \right| I_9$ .

Analysis:  $11,26^{\circ}/_{0}$  Co;  $58,03^{\circ}/_{0}I$ ;  $14,06^{\circ}/_{0}N$ ; calculated:  $11,30^{\circ}/_{0}$  Co;  $57,96^{\circ}/_{0}I$  and  $14,21^{\circ}/_{0}N$ .

Besides this compound, also a small quantity of crystals of  $\{Co(E\"{i}ne)_3\}I_3+1H_2O$  was isolated. (See here-after).

Crystal-form of 
$$\left| Co_3 \frac{(E\"{i}ne)_6}{(Triam)_2} \right| I_9$$
.



On slow evaporation of a solution of the salt in water at room-temperature thick, dark coloured, very lustrous crystals are deposited (Fig.  $4^{\rm A}$ ). From a hot solution, however, on slow cooling long blood-red needles (Fig.  $4^{\rm B}$ ) are obtained.

## Rhombic-bisphenoidal. a:b:c=0.6498:1:0.9959.

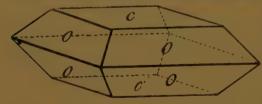
Forms observed:  $c = \{001\}$ , either predominant or small, as in Fig. 4<sup>B</sup>, but always very lustrous. In the larger crystals, the face c appears to to be finely striated parallel to c: b, giving multiple reflexions. Further:  $m = \{110\}$ , strongly lustrous;  $a = \{100\}$  and  $b = \{010\}$ , both yielding good images, on b commonly better than on a;  $0 = \{111\}$ , narrow, always present, giving very sharp reflexions;  $0' = \{111\}$  much broader than 0, sometimes equally broad, yielding sharp images;  $q = \{021\}$ , only present in the larger crystals and then very well reflecting;  $\omega = \{1.1.10\}$  and  $\omega' = \{1.1.10\}$ , extremely narrow. The crystals formed at lower temperatures are more tabular parallel to c; those developed at higher temperatures are more elongated parallel to the c-axis. These

crystals exhibit often, very narrow,  $p = \{520\}$  and show a hemihedral habitus. The vertical zône is often badly built; however, in the needle-shaped crystals much better than in those drawn in Fig. 4<sup>A</sup>. Rarely very beautifully shaped crystals, as reproduced in Fig. 4<sup>C</sup>, were observed. The angular values differ often rather appreciably in different individuals, as this is often observed with mixed crystals.

Angles:	Observed	1:	Calc	rulated
a:m=(100):(110)	=* 33°	1'	-	
c:o = (001):(111)	=* 61	19	-	_
o: m = (111): (110)	= 28	41	28°	41'
b: m = (010): (110)	= 56	55	56	59
a:p = (100):(520)	= 14	31	14	34
$c:\omega = (001):(1.1.16)$	0) == 10	24	- 10	211/2
m:p = (110):(520)	= 18	23	18	27
a:o = (100):(111)	= 42	40	42	$33^{1}/_{2}$
c:q=(001):(021)	= 63	21	63	201/2
m:q=(110):(021)	= 60	44	60	511/2
$o:o'=(111):(1\overline{1}1)$	= 57	15	57	$6^{2}/_{3}$
$o: o' = (111): (\overline{1}11)$	= -	-	94	43
$o: \omega = (111): (1.1.1)$	0) = 50	59	50	571/2

Cleavage parallel to b. On a, m and b everywhere normal extinction: the optical axial plane is  $\{001\}$ . Strongly dichroitic: on m for vibrations perpendicular to the c-axis blood-red, for those perpendicular to the first: orange-yellow.

From the solution, as already said before, besides this iodide, also



obtained, which were readily measurable (Fig. 5).

small, pyramidal crystals were

Rhombic-bipyramidal.

a:b:c=0.8538:1:0.8625.

Forms observed:  $c = \{001\}$  and  $o = \{111\}$ , yielding good reflexes; the habitus of the crystals is often apparently hemimorphic.

## Fig.5

Angular	Values:	Observed:	Calculated:
c:0	= (001) : (1	$11) = 53^{\circ}  1^{1/2'}$	
0:0	= (111) : (1	$\overline{11}$ ) = 62 30	_
0:0	$= (111) : (\overline{1})$	11) = 74 46	74° 50′

No distinct cleavability was observed.

The axial plane is {010}, with the c-axis as the first bissectrix. The axial angle is small: no appreciable dichroism.

Evidently these crystals are really identical with those of {Co(Eine)<sub>3</sub>} I<sub>3</sub>

 $+1H_2O$ . Analysis also showed this to be the case:  $59.7\,^{0}/_{0}\,I$ ;  $9.24^{0}/_{0}\,C_{0}$ ; and  $13.2\,^{0}/_{0}\,N$ . This fact proves once more, that, as stated, the complex ion of the diethylenediamine-chloro-aquo-cobaltic-salts is partially decomposed, if its solution is boiled with dilute solutions of bases, under formation of the apparently very stable triethylenediamine-derivatives.

Also another derivative of the new threefold ion was obtained in magnificent crystals by heating of diethylenediamine-chloro-aquo-cobaltic-

sulphate:  $\left\{ \begin{array}{c} (Eine)_2 \\ Co \\ H_2O \end{array} \right\} SO_4 + 1^1/_2 H_2O$ , with a solution of the base and

treating the solution thus prepared with  $Ag_2SO_4$ , for the purpose of eliminating all Cl-ion from the liquid.

If 27,53 grams of the complex sulphate mentioned above be boiled during four hours under reflux with 7,5 grams of the base (in  $11^{\circ}/_{\circ}$  solution), first a beautifully crystallised salt is deposited, appearing in brown-red octahedral crystals; if the solution after evaporation and after all chlorosulphates formed in this reaction are by means of  $Ag_2SO_4$  transformed into sulphates, is cooled down to room-temperature, the new salt is readily deposited. Sometimes this salt is also obtained in good quantity, before the solution is treated with  $Ag_2SO_4$ : thus, for instance, in a reaction between 31,7 grams of the chloro-aquo-sulphate and 8,64 grams of the base (in  $10^{\circ}/_{\circ}$ -solution), immediately 12 grams of the pure salt were, on cooling, deposited in beautiful, lustrous crystals. It is better, however, to treat the solution first with  $Ag_2SO_4$  so that all Cl-ion is eliminated from the liquid. In that case the new compound is directly obtained in lustrous crystals, besides a mother-liquor B.

The new sulphate was recrystallised several times and then analysed.

Analysis:  $5.79^{\circ}/_{0}$   $H_{2}O$ ; calculated for  $Co_{3}$   $\frac{(Eine)_{6}}{(Triam)_{2}}/_{2}$   $(SO_{4})_{9}$   $+8H_{2}O$ :  $Co_{3}$   $Co_{4}$   $Co_{5}$   $Co_{5}$ 

 $(SO_4)$ ; 22,30  $^{\circ}/_{0}$  N; calculated for the anhydrous sulphate: 14,03  $^{\circ}/_{0}$  Co; 34,28  $^{\circ}/_{0}$   $(SO_4)$  and 22,22  $^{\circ}/_{0}$  N.

The cryoscopical determination of the molecular weight gave results, which were in close agreement with the constitution mentioned above. If the sulphate in dilute solution were completely dissociated, each molecule would give 11 ions; therefore, instead of the normal molecular weight: 2666 for the hydrate, or 2522 for the anhydrous salt, — values could be experted to be found in this case, oscillating round 242. Now a solution of 0,4610 grams of the substance in 30,829 grams water, showed a depression of the freezing-point of:  $0^{\circ}$ ,100 C. The solution contained 1,495  $^{\circ}$ /<sub>0</sub> (or 1,414  $^{\circ}$ /<sub>0</sub> of the anhydrous) salt; therefore, the apparent molecular weight is here: 261,6, corresponding to a real molecular weight of 2877. The degree of dissociation  $\alpha$  thus would be about 0,85 at this concentration; it seems from conductivity-experiments, that even a lower degree of dissociation is present here.

Some measurements of the electric (molecular) conductivity gave the following results:

Concentration in grams per Liter	Concentration in Mols. per Liter	Dilution in Liters	Specific conductivity (× 104)	Mol .con- ductivity (× 104)	Degree of dissociation
46.024	0.01879	53.22	22.74	1210	0.43
34.518	0.01295	77.22	18.09	1397	0.50
25.889	0.00971	102.98	14.08	1450	0.52
19.416	0.00728	137.36	11.27	15 <del>4</del> 8	0.55
14.562	0.00546	183.15	8.92	1635	0.59
7.281	0.00273	366.30	4.92	1802	0.65
0.244	0.00009	10989	0.252	2769	1.0

The last mentioned value of the molecular conductivity (2769) may be considered as giving practically the value of the conductivity at an infinite dilution. This number is extremely high: for salts with 2 ions,  $\mu_{\infty}$  commonly is of the order: 140; for such with 3 ions: 250; for such with 4 ions: 410; for salts with 5 ions: about 560; etc. On extrapolation, — this being, of course, always somewhat hazardous, — for a salt with 6 ions,  $\mu_{\infty}$  would be of the order: 750; for those with 8 ions, of the order: 1100; for a salt with 9 ions: about 1400; for such with 10 ions, of the order: 1600; while for salts with 11 ions, the value of  $\mu_{\infty}$  would be situated in the neighbourhood of 1800. Uncertain as these data may be, it must be clear in every case, that the number of ions produced here, is abnormally large.

On my demand, professor KRUYT was kind enough to determine the specific coagulating power of the complex cation of this new kind of salts, with the purpose to draw nearer conclusions about its valency. The influence of this cation, in the form of its chloride, on a colloidal solution of  $As_2S_3$ , in comparison with that of a three- and a six-valent cation of analogous constitution, was studied in this respect. It appeared, that while 100 mille-mols of the 6-valent ion were necessary to provoke flocculation, here only 32 mille-mols were sufficient for the same result. From this the conclusion may be drawn, that without any doubt the valency of the new complex ion is in every case higher than six. This fact also may serve as an argument to corroborate the conclusion, that the new complex ion is really a nine-valent one; moreover, the analysis of the corresponding salts must eliminate all doubt whatever about the correctness of this view.

Crystal-form of Hexa-ethylenediamine-Ditriaminotriethylamine-tricobalticsulphate:  $Co_3(Eine)_6 \ (SO_4)_9 + 8H_2O$ .

This compound crystallizes on slow evaporation from its aqueous solutions

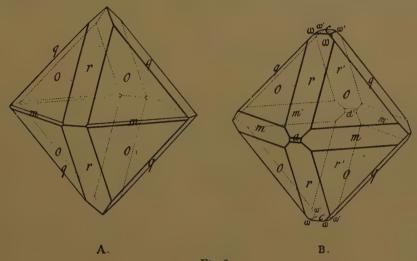


Fig. 6

in big, brown-red crystals with octahedral habit. They possess very lustrous facets and allow accurate measurements to be made.

Rhombic-bipyramidal; pseudo-tetragonal.  

$$a:b:c=1,0131:1:1,1277.$$

Forms observed:  $o = \{111\}$ , large and predominant;  $r = \{101\}$  and  $q = \{011\}$ , broad and lustrous;  $m = \{110\}$ , narrower but yielding sharp reflexions. Sometimes are found also:  $a = \{100\}$ , small;  $c = \{001\}$ , very small;  $\omega = \{113\}$ , small, but well measurable. The aspect of the crystals is often that of octahedra, combined with a rhombododecahedron; sometimes m is absent, sometimes also a, c and  $\omega$  are lacking.

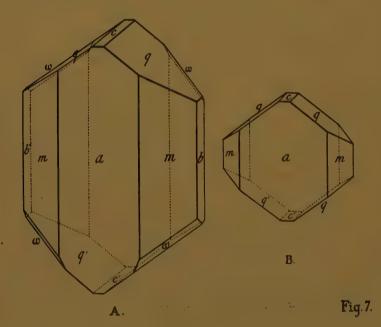
Angular Values:	Obse	erved:	Calcu	lated: '
o:q = (111)	: (011) =* 36	° 26 <sup>1</sup> / <sub>4</sub>	-	-
o:m = (111)	: (110) =* 32	$15^{1}/_{2}$	-	-
o:o = (111)	$: (\overline{1}11) = 73$	53 <sup>1</sup> / <sub>2</sub>	73°	53′
o:o = (111)	$: (1\overline{11}) = 64$	32	64	31
o:o = (111)	$(1\overline{1}1) = 72$	53	72	$52^{1}/_{2}$
o: r = (111):	: (101) = 36	$56^{1}/_{2}$	36	$56^{1}/_{2}$
r:r = (101)	$(10\overline{1}) = 84$	. 4	83	52
m:m = (110):	$(1\overline{10}) = 90$	46	90	45
q:q=(011):	$(0\overline{1}1) = 96$	.45	96	52
$q:r = (0\overline{1}\overline{1})$	$(10\overline{1}) = 63$	32	63	41

Angular	Values:	Obs	erved:	Calc	ulated :
$\epsilon:m$	$=(1\overline{01})$	: (110) = 58	28	58	291/2
m : q	= (110) :	(011) = 57	40	57	491/2
0:0	= (111)	$(\overline{11}\overline{1})=107$	$6^{1/2}$	107	$6^{1/2}$
C: 60	= (001)	(113) = 27	48	27	$50^{1}/_{2}$
ω: ο	= (113)	(111) = 30	$6^{1/2}$	29	54
a: m	= (100)	(110) = 45	33	45	221/2
a: r	= (100)	(101) = 42	2	41	56
r:c	= (101)	(001) = 48	8	48	4

No distinct cleavage was observed.

The crystals are optically biaxial; the axial plane is obviously  $\{001\}$ , with the b-axis as  $1^{\rm st}$  bissectrix. The double refraction is positive; weak dispersion, with rhombic character and  $\varrho < v$ . The apparent axial angle is rather large. No appreciable dichroism is present.

 $\S$  4. On evaporation at room-temperature the mother-liquor B gave firstly another crop of the crystals described in the above; afterwards it became more and more viscous and gave some fractions consisting of crystals, which on recrystallisation and slow evaporation of their solutions yielded measurable crystals of the form reproduced in Fig. 7.



Although giving good images, these crystals showed angular values, which were oscillating within rather wide limits:

$$a: c = 83^{\circ} 18' - 83^{\circ} 43'.$$
  
 $a: q = 84^{\circ} 36' - 84^{\circ} 58'.$   
 $c: q = 36^{\circ} 12' - 36^{\circ} 27',$ 

Therefore, the axial ratio of these monoclinic-prismatic crystals varied between:

a: 
$$b: c = 0.7421: 1: 0.7371; \beta = 83^{\circ} 18'$$
  
and  $a: b: c = 0.7415: 1: 0.7431; \beta = 83^{\circ} 43'.$ 

They give the impression of being mixed crystals with a varying content of the isomorphous admixtures. Indeed, analysis taught us, that here very probably mixed crystals are present, principally of triethylene-diamine-cobaltic-sulphate:  $\{Co(Eine)_3\}_2(SO_4)_3+2H_2O$  with a small quantity of ditriamino-triethylamine-cobaltic-sulphate:  $\{Co(Triam)_2\}_2(SO_4)_3+2H_2O$ , and probably also of a threefold complex ion with  $6H_2O$ . Analysis gave;  $13.2\,^0/_0$  Co;  $35.2\,^0/_0$  ( $SO_4$ );  $17.0\,^0/_0$  N in the anhydrous substance, while the hydrate contained:  $3.78\,^0/_0$  H<sub>2</sub>O. For the salts already mentioned, the data for the different anhydrous substances are:

$\left\{ \text{Co}(\text{Eine}_3) \right\}_2 (\text{SO}_4)_3$ :	$\left\{ \text{Co}(\text{Triam})_2 \right\}_2 (\text{SO}_4)_3$ :	Co <sub>3</sub> (Eine) <sub>6</sub> (SO <sub>4</sub> ) <sub>9</sub> :
15,40/0 C <sub>0</sub>	11,9º/ <sub>0</sub> C <sub>0</sub>	14,03 <sup>0</sup> / <sub>0</sub> C <sub>0</sub>
37,6 <sup>0</sup> / <sub>0</sub> (SO <sub>4</sub> )	29,1 <sup>0</sup> / <sub>0</sub> (SO <sub>4</sub> )	34,28 <sup>0</sup> / <sub>0</sub> (SO <sub>4</sub> )
21,90/ <sub>0</sub> N	22,7º/ <sub>0</sub> N	22,22º/ <sub>0</sub> N
and for $2H_2O: 4.50/_0$	for $2H_2O: 3.50/0$	for $6H_2O: 4,10/_0$

After fractional crystallisation, renewed determinations gave:  $14.6^{\circ}/_{0}$  Co;  $36.1^{\circ}/_{0}$  ( $SO_{4}$ );  $22.0^{\circ}/_{0}$  N; and also:  $4.0^{\circ}/_{0}$   $H_{2}O$ . These data are somewhat closer to the composition of the first mentioned salt than the former. After transformation of the salt into the corresponding *iodide* there, was found in the anhydrous salt:  $60.83^{\circ}/_{0}I$ ; calculated for  $\{Co(E\"{ine})_{3}\}I_{3}$ :  $61.4^{\circ}/_{0}I$ ; the threefold complex salt would have given  $58^{\circ}/_{0}I$ , while for  $\{Co(Triam)_{2}\}I_{3}$ , only:  $52^{\circ}/_{0}I$  is calculated.

From the last but one fraction of the mother-liquor also a small amount of a beautifully crystallized *iodide* was deposited, whose analysis gave:  $2.89\,^0/_0\,H_2O$ , while in the anhydrous substance:  $61.81\,^0/_0\,I$  was present. Here certainly no other product than  $\{Co(Eine)_3\}\,I_3+1H_2O$  has occurred. In a *iodide* from the last mother-liquor, finally, we found:  $3.8\,^0/^0\,H_2O$  and  $56.8\,^0/_0\,I$ ; so that in this case again undoubtedly a mixture of the last salt with one or more of the other *iodides* must be supposed to have been present.

The measurements of the crystals reproduced in Fig. 7, gave the following results: forms observed:  $a = \{100\}$ , predominant and highly lustrous;  $m = \{110\}$ , mostly large and yielding excellent reflexes, but

sometimes smaller;  $q = \{011\}$ , very lustrous and well developed;  $c = \{001\}$ , mostly small, but well reflecting;  $b = \{010\}$ , only narrow;  $\omega = \{\overline{121}\}$ , mostly present with only two parallel faces, but yielding excellent images.

Angular Values:	Observed:	Calculated:
a:c = (100):(001) = *83°	18' — 83° 43'	-
a: m = (100): (110) = *36	231/2	_
c: q = (001): (011) = *36	$12^{1}/_{2}$ — 36 27	
$q:\omega = (011):(\overline{1}21) = 36$	52	36° 51′
$\omega: m = (\overline{1}21): (\overline{1}10) = 36$	56	36 471/2
a:q=(100);(011)=84	36 84 58	84 36—84 57
m: q = (110): (011) = 64	45	64 57
$m:q=(\overline{1}10);(011)=73$	48	73 381/2
m:b = (110):(010) = 53	371/2	53 361/2
b:q=(010):(011)=53	33	53 33
$a:\omega = (100):(\overline{1}21) = 63$	221/2	63 25
$b: \omega = (010): \overline{(121)} = 42$	71/2	42 4

No distinct cleavability was stated.

On  $\{100\}$  the optical extinction is parallel and perpendicular to a:m; the plane of the optical axes is  $\{010\}$ , while on  $\{100\}$  one of the axes emerges at the border of the field of the microscope.

As a control, we prepared some pure triethylenediamine-cobaltic-sulphate; however this salt could not be obtained in measurable crystals. As a further argument in favour of the supposition of mixed crystals being produced in this case, also the following data may be taken into account. If a solution of the salt of the threefold complex ion, as it is

obtained in the reaction between triamino-triethylamine and  $C_{I}^{(Eine)_2}$  (SO<sub>4</sub>)

 $+1\frac{1}{2}H_2O$ , — is treated with an insufficient 1) quantity of  $Ag_2SO_4$ , then, after crystallisation of the complex sulphate, crystals of a paler coloured compound are deposited from the viscous residual mother-liquor; which crystals, besides  $(SO_4)$ , also contain ionogenic chlorine and have

according to the analysis, the composition:  $Co_3(Eine)_6/(Cl_{12}+10H_2O.$ 

Analysis: In the anhydrous salt was found:  $14.81^{\circ}/_{0}$  Co;  $18.1^{\circ}/_{0}$  Cl;  $12.5^{\circ}/_{0}$  (SO<sub>4</sub>) en  $23.92^{\circ}/_{0}$  N; calculated:  $14.9^{\circ}/_{0}$  Co;  $17.96^{\circ}/_{0}$  Cl;  $12.14^{\circ}/_{0}$  (SO<sub>4</sub>);  $23.60^{\circ}/_{0}$  N. In the hydrate itself:  $13.77^{\circ}/_{0}$  Co;  $16.50^{\circ}/_{0}$  Cl;  $11.72^{\circ}/_{0}$  (SO<sub>4</sub>) and  $6.95^{\circ}/_{0}$  H<sub>2</sub>O; calculated for the above formula:  $13.87^{\circ}/_{0}$  Co;  $16.68^{\circ}/_{0}$  Cl;  $11.30^{\circ}/_{0}$  (SO<sub>4</sub>); and  $7.05^{\circ}/_{0}$  H<sub>2</sub>O.

<sup>1)</sup> It is very remarkable that these salts manifest such a strong tendency to form chlorosulphates, if circumstances are favourable: in these salts  $^{2}$ /<sub>3</sub> of the ionogenic bonds are substituted by halogen-atoms.

Crystal-form of 
$$\left\{ Co_3 \frac{(Eine)_6}{(T riam)_2} \right\}_{2(SO_4)_3}^{Cl_{12}} + 10 H_2O.$$

Small, beautifully shaped, very lustrous crystals of a steep rhombo-

hedral habit; they always exhibit the forms *R*, *r* and *s*, and have the paler colour of the *luteo*-salts. (Fig. 8).

Ditrigonal-scalenohedral. 
$$a = 51^{\circ} 10'$$
;  $a : c = 1 : 3,0114$ .

All three kinds of facets give very sharp reflexes:  $R = \{100\} = \{10\overline{1}1\}$ , strongly predominant;  $r = \{110\} = \{01\overline{1}2\}$ , truncating the polar edges of R symmetrically:  $s = \{211\} = \{10\overline{1}4\}$ , small, but well developed.

	· · ·				
	Angular values:	Observed	d:	Calcula	ited:
)	$s_1: s_2 = (211): (121)$	=* 69°	21'	-	-
	$s_1: r_3 = (211): (011)$	= 101	14	101°	92/3
	$R_1: r_1 = (100): (110)$	= 56	15	56	20
	$R_1: R_2' = (100): (\overline{010})$	= 67	30	67	20
	$R_1: s_1 = (100): (211)$	= 32	56	32	<b>53</b> <sup>1</sup> / <sub>3</sub>
	$R_1: r'_3 = (100): (\overline{011})$	= 45	49	45	57
	$r_1: r_2 = (110): (101)$	= 51	30	51	22
	$r_1: s_1 = (110): (211)$	= 48	42	48	39
	$r_1: r_2' = (110): \overline{(101)}$	= 82	36	82	42

No distinct cleavability could be found,

R

Fig.8.

A section perpendicular to the optical axis in convergent polarized light exhibits the normal axial image of an uniaxial crystal without circular polarisation. The optical character is negative.

In preparing the triethylenediamine-cobaltic-sulphate from the corresponding chloride by means of  $Ag_2SO_4$ , the tendency to form such a chlorosulphate of the composition:  $\left\{ Co\left(Eine\right)_3 \right\}_{2}^{Cl_4} + 5H_2O$  manifested itself again very clearly.

Analysis: The hydrate contained:  $11.48^{\circ}/_{0} H_{2}O$ ; calculated for  $5H_{2}O$ :  $11.16^{\circ}/_{0} H^{2}O$ . In the anhydrous salt we found:  $16.72^{\circ}/_{0}Co$  and  $19.40^{\circ}/_{0}Cl$ ; calculated:  $16.48^{\circ}/_{0} Co$  and  $19.84^{\circ}/_{0} Cl$ . Also this chlorosulphate crystallized exceedingly well (Fig. 9).

Crystal-form of 
$$Co(Eine)_3$$
  $Cl_4 + 5 H_2O$ .

The substance appears in beautiful, light-brown, rhombohedral crystals.

Ditrigonal-scalenohedral.  $\alpha = 51^{\circ} 0'$ : a: c = 1:3.0285. Forms observed:  $R = \{100\} = \{10\overline{1}1\}$ , predominant;  $r = \{110\} = \{01\overline{1}2\}$ .

narrow, but sharply reflecting;  $s = \{211\}$  =  $\{10\overline{1}4\}$ , well developed and yielding good reflections.

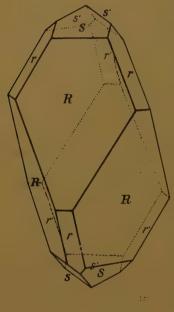


Fig.9

Angular values: Observed: Calculated:  

$$R: R = (100): (\overline{010}) = 67^{\circ} 15^{1/2} -$$
  
 $R: r = (100): (110) = 56 22 56^{\circ} 22^{1/4}$   
 $R: s = (100): (211) = 32 50 32 53$   
 $s: s = (211): (121) = 69 36 69 22$ 

No distinct cleavability could be stated. The crystals are uniaxial, negative, without circular polarisation; they are evidently completely isomorphous with the *chlorosul-phate* of the threefold complex ion, crystallizing with  $10\,H_2O$ , although the different composition is clear enough by the data of the analysis in both cases. Regarding this isomorphism between both kinds of crystals, it appears highly probable, that also the monoclinic crystals described before, are

really mixed crystals, which for the greater part consist of triethylene-diamine-sulphate. If, — as from the data of analysis seems highly probable, — in the reaction considered in the above also  $Co(Triam)_2$  is produced, the totality of all reactions might be described by an equation of the form:

$$60 \left\{ Co \frac{(E\ddot{\imath}ne)_{2}}{Cl} \left\{ (SO_{4}), 1^{1}/_{2} H_{2}O + 40 N (CH_{2} \cdot CH_{2} \cdot NH_{2})_{3} = \right. \right.$$

$$= \left\{ Co_{3} \frac{(E\ddot{\imath}ne)_{6}}{(Triam)_{2}} \right\}_{2} (SO_{4})_{9}, 8 H_{2}O + \left\{ Co_{3} \frac{(E\ddot{\imath}ne)_{6}}{(Triam)_{2}} \right\}_{2} (SO_{4})_{3}, 10 H_{2}O + \right.$$

$$+ 8 \left\{ Co (E\ddot{\imath}ne)_{3} \right\}_{2} \frac{Cl_{4}}{(SO_{4})}, 5H_{2}O + 8 \left\{ Co (E\ddot{\imath}ne)_{3} \right\}_{2} (SO_{4})_{3}, 2 H_{2}O + \right.$$

$$+ 16 \left\{ Co (Triam)_{2} \right\}_{2} \frac{Cl}{(SO_{4})}, x H_{2}O + (76-16x) H_{2}O.$$

In this equation the fact of the decomposition of the diethylene-diamine-chloro-aquo-cobaltic ion is simultaneously included. It appears possible to control the exactness of this equation; for if the original solution obtained is treated with  $Ag_2SO_4$ , all compounds present are transformed into the corresponding sulphates. If now all sulphate of the threefold complex ion is allowed to depose, and then the salts of the

residual mother-liquor is precipiated in the form of *iodides*, the precipitate thus obtained must exclusively consist of  $\{Co(Eine)_3\}I_3$ ,  $1H_2O$ , because the corresponding salts of the ion:  $\{Co(Triam)_2\}^{\cdots}$  are so soluble, that they are not precipitated by any reagent, — not even by a solution of  $NaI_*$ . According to the equation mentioned above, it should be expected, that the quantity of the salt of the threefold complex ion will be 0,25 of the total weight of the original quantity of the *chloro-aquo-salt* used, while on each gram of the threefold complex salt (as sulphate), 3,83 grams of *triethylene-diamine-cobaltic-jodide* should be generated.

In the experiment itself 6,3 grams chloro-aquo-salt were treated in the way described above with 1,73 grams of triaminotriethylamine (24 cm<sup>3</sup> of a solution) and 50 grams of water, transformed in sulphate by means of  $Ag_2SO_4$ ; then the threefold sulphate was separated from the solution, and the strongly concentrated mother-liquor precipitated with NaI.

The recrystallised salts were weighed separately. It was found, that from 6,3 grams of the *chloro-aquo-salt*, 1,65 grams *sulphate* of the threefold complex ion were obtained; and from the mother-liquor 5,90 grams of the *iodide*; calculated: 1,57 grams of the *sulphate* and 6,03 grams of the *iodide*. Considering the inevitable experimental inaccuracies of the method, the given equation represents, therefore, indeed a fairly good scheme of the reaction taking place here.

From the analytical data given in the above, it must be clear, that here no compounds are present of a type to be expected, if the base used were *tetra*valent in coordinative respect. Neither salts of the type:

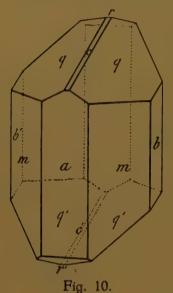
numerous analyses mentioned above. The nitrogen-determinations are, in first instance, of interest in this respect. Therefore, we think it to be beyond any doubt, that in the type of salts here produced, *triamino-triethylamine* exhibits the function of a *tri*valent, not of a *tetra*valent substitute in coordinative respect.

§ 5. With the purpose of characterizing somewhat more precisely the derivatives of the new threefold complex ion, we have prepared a series of other salts, e.g.: the corresponding nitrate, chlorate, perchlorate, iodate, rhodanide and dithionate. By double decomposition of the sulphate by means of the barium-salts of the corresponding acids, most of these salts may be readily obtained. The rhodanide appeared too little soluble, as to obtain other crystals than only microscopically small, brown-red tables; the iodate, on the contrary, is much too soluble and its solutions on slow evaporation were always transformed into a brown-red resinous mass, which showed no tendency at all to crystallize. The chlorate is also very soluble and crystallizes in thin, scarcely measurable needles.

The rather well soluble *nitrate*, and also the *perchlorate* could, however, be obtained in big, beautiful crystals; the *dithionate*, which is far more soluble in hot water than in cold, was by slow evaporation of its solution finally obtained in well measurable crystals.

All salts were analysed: the *nitrate* appears to contain  $4H_2O$ , the *perchlorate*:  $6H_2O$ , and the *dithionate*, notwithstanding its spare solubility in cold water,  $18H_2O$ . The crystal-forms of these compounds are in the following described in all necessary details.

Crystal-form of 
$$Co_3 \frac{(Eine)_6}{(Triam)_2} (NO_3)_9 + 4H_2O$$
.



From a hot, very concentrated solution of the salt great brown-red crystals are obtained, which have the shape of Fig. 10.

Monoclinic-prismatic.

$$a:b:c=1,2327:1:0,5582$$
  
 $\beta=64^{\circ}34'$ 

Forms observed:  $a = \{100\}$ ,  $b = \{010\}$ ,  $m = \{110\}$  and  $q = \{011\}$ , all about equally well developed and yielding good reflections;  $r = \{201\}$ , smaller than q, but highly lustrous;  $c = \{001\}$ , extremely narrow, gives feeble images and is often totally absent. The habit is short-prismatic parallel to the c-axis, or somewhat elongated in the direction of the a-axis.

Angular values: \	Observ	ed:	Calculated:
a:m=(100)	(110) =*48°	4'	_
b: q = (010)	(011) = *63	15	
m:q=(110)	(010) = *53	<b>4</b> 6	_
q: r = (011)	(201) = 57	38	57° 41¹/2′
a: r = (100)	$(20\overline{1})=62$	19	62 12
q:q=(011)	$(0\overline{1}1) = 53$	30	53 30
c;q=(001)	(011) = 26	50	26 45
b: m = (010)	(110) = 41	56	41 56
$\mathbf{a}:\mathbf{q}=(100)$	(011) = 67	35	67 35
$\boldsymbol{a}:\boldsymbol{c}=(100)$	(001) = 64	44	64 34
c: r = (001)	(201) = 53	25	53 14

No distinct cleavage was observed.

Analysis gave:  $3.68 \, {}^{\circ}/_{0} \, H_{2}O$ ; calculated:  $3.75 \, {}^{\circ}/_{0} \, H_{2}O$ .

Crystal-form of 
$$\left\{ Co_3 \frac{(Eine)_6}{(Triam)_2} \right\} (ClO_4)_9 + 6 H_2O$$
.

From a solution of the *perchlorate* in water big crystals are deposited on slow evaporation at room-temperature, which exhibit a long-prismatic,

or rarely a tetrahedrical, habit. (Fig. 11).

Rhombic-bipyramidal; in some cases with an apparent bisphenoidal development.

$$a:b:c=1,1750:1:0,5619.$$

Forms observed:  $m = \{110\}$ ,  $r = \{101\}$  and  $q = \{011\}$  yield all very sharp images;  $p = \{120\}$ , however, is very narrow, but well measurable;  $a = \{100\}$  is scarcely visible and gives very feeble reflections.

Angular Values:	Obs	erved:	Calculated	d
m:r=(110):(101)	=*73°	$45^{1}/_{2}'$	_	
m: q = (110): (011)	=*68	6		
r: q = (101): (011)	= 38	$8^{1}/_{2}$	38° 81/2'	
$m: m = (110); (1\overline{1}0)$	= 99	12	99 12	
$q: q = (011): (0\overline{1}1)$	= 58	42	58 40	
a:p=(100); (210)	== 30	43	30 26	
p:m=(210):(110)	= 19	1	19 10	

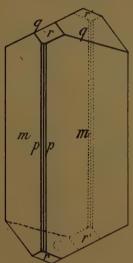


Fig. 11.

Sometimes, moreover, a form {140}, although extremely narrow, was observed. No distinct cleavability could be found.

The optical axial plane is  $\{001\}$ ; on m one of the optical axes is visible. Strongly dichroitic: on m for vibrations parallel to the c-axis yellow, for those perpendicular to it, orange-red.

Analysis gave:  $6,00^{\circ}/_{0}$   $H_{2}O$ ; calculated:  $5,91^{\circ}/_{0}$   $H_{2}O$ .

Crystal-form of 
$$Co_3 \frac{(E\ddot{\imath}ne)_6}{(Triam)_2} \left( (S_2O_6)_9 + 18H_2O. \right)$$

From a cold, saturated solution small, yellow-brown crystals are deposited on slow evaporation, which show lustrous planes. (Fig. 12).

$$a:b:c=1,7232:1:1,0902.$$
 $A=108^{\circ}\ 16'.$ 
 $a=115^{\circ}\ 7^{1}/_{2}'.$ 
 $B=117^{\circ}\ 53'.$ 
 $\beta=122^{\circ}\ 34'.$ 
 $C=82^{\circ}\ 46'.$ 
 $\gamma=71^{\circ}\ 3^{1}/_{3}'.$ 

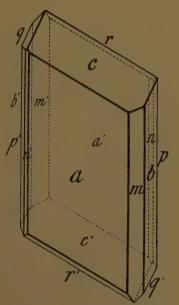


Fig.12

Forms observed:  $a = \{100\}$ , mostly the broadest of all forms and very lustrous;  $b = \{010\}$ , narrower, but, just as  $c = \{001\}$ , yielding very sharp reflections;  $m = \{110\}$  gives also very good images;  $p = \{110\}$  and  $n = \{210\}$ , extremely narrow and allowing only approximate measurements;  $q' = \{011\}$ , narrow, well measurable;  $r = \{101\}$  and  $s = \{201\}$ , extremely narrow, often absent.

Angular Values:	Observ	ed:	Calcul	ated:
a:c=(100):	(001) =* 62°	7′	_	
c:b=(001):	(010) = 71	44.	_	
a:b=(100):	(010( =* 97	14	. –	
a: m = (100):	(110) =* 63	22	_	
b: q' = (010):	(011) =* 55	17	_	
m: b = (110):	(010) = 33	52	33°	52′
$q': c' = (01\overline{1}):$	(001) = 52	59	52	59
b:p=(010):	$\overline{(110)} = 29$	30	28	13
$p: n = (\overline{110}):$	$(\overline{2}10) = 16$	36	16	55
n : a' = (210) :	(100) = 36	40	37	38
c:r=(001):	$\overline{(101)} = 38$	5	38	27
$\mathbf{r}:\mathbf{s}=(\overline{10}1):$	(201) = 31	33	31	28
$s:a=(\overline{201}):$	(100) = 48	15	47	58

The crystals show no distinct cleavage, but they are very brittle. Analysis gave:  $9.52\,^0/_0$   $H_2O$  and  $11.74\,^0/_0$  Co; calculated:  $9.47\,^0/_0$   $H_2O$  and  $11.45\,^0/_0$  Co. In the anhydrous salt was found:  $10.58\,^0/_0$  Co; calculated:  $10.35\,^0/_0$  Co.

§ 6. In no case any indication of the generation or presence of isomeric salts was ever observed; evidently each product obtained was wholly homogeneous, there being only salts produced of one and the same spatial configuration. However, it was now the question, whether these salts were decomposable into optical antipodes or not; and if so, whether perhaps several racemic salts, — mutually isomorphous in that case, — were giving mixed-crystals of the [shapes observed here, or whether these crystals represented really one and the same compound? In the first case, several optically-active compounds would possibly be found as final terms of the fractional crystallisation-experiments; in the latter case, only a single dextrogyratory and a single levogyratory antipode whould be met with.

Preliminary experiments first seemed to indicate really the possibility of such a fission by the aid of d-tartaric acid; afterwards, however, it could be proved, that this was not the case. For the purpose of executing the fission desired, a quantity of the sulphate was first transformed into the  $iodide: \left\{ Co_3 \frac{(Eine)_6}{(Triam)_2} \right\}$ , which was thoroughly purified by repeated crystallisation from hot water.

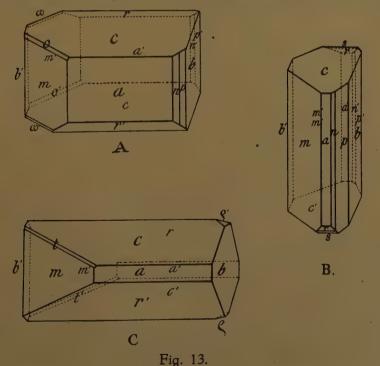
Totally 28,95 grams of the pure *iodide* were thus obtained and by means of 16 grams pure *silver-d-tartrate* they were transformed into an *iodo-tartrate*, having the composition:  $\begin{cases} C_{03} & (Eine)_6 \\ C_{03} & (Triam)_2 \end{cases} & (C_4 H_4 O_6)_3 \end{cases}$  because it was shown by preliminary tentatives, that this *iodo-tartrate* amongst all had the greatest power of crystallisation. The solution was concentrated on the water-bath, until it became viscous (about 50 ccm.); after 36 hours, crusts of beautifully lustrous, intergrown, brown-red crystals were deposited, weighing 10,75 grams. Analysis proved them to contain 3  $H_2O$ :  $3,23^0/_0 H_2O$ ; calculated:  $3,19^0/_0 H_2O$ . The hydrate contains:  $22,6^0/_0 I$ ; calculated:  $22,3^0/_0 I$ . The solution appears to be dextrogyratory.

Cristal-form of 
$$\left| Co_3 \frac{(E\"{i}ne)_6}{(Triam)_2} \right| \frac{I_3}{d-(C_4H_4O_6)_3} + 3 H_2O$$
.

Beautifully developed, often intergrown and then only occurring in rudimentary individuals, brown-red, very lustrous crystals, showing constant angular values. With some simple magnificent individuals the following measurements were made.

> Monoclinic-sphenoidal. a:b:c=0.7226:1:0.9192; $\beta=56^{\circ}35^{1}/4'.$

Forms observed:  $a = \{100\}$ , well developed and lustrous;  $c = \{001\}$ ,



large, highly lustrous, yielding ideal images, just as  $m = \{\overline{1}10\}$ ,  $b = \{010\}$ , broad and very lustrous;  $b = \{0\overline{1}0\}$ , mostly narrow, sometimes broader, but always yielding good reflections;  $r = \{\overline{1}01\}$ , rather broad and well reflecting;  $s = \{\overline{1}02\}$ , much narrower than r, often absent, well reflecting;  $p = \{120\}$ , mostly narrow, sometimes broader, a little dull;  $n = \{110\}$ , mostly absent, sometimes equally broad as p, yielding sharp reflections, but somewhat duller than m;  $\omega = \{\overline{1}11\}$ , often absent, narrow;  $o = \{\overline{221}\}$ , broader than  $\omega$ , often absent, but yielding good images. The habit of the crystals is rather elongated parallel to the b-axis, or short-prismatic parellel to the c-axis. (Fig. 13).

Angles:	Obs	ervec	l:	Calcu	lated :
c: m = (001): (110)	=*	61°	52'	_	-
$c: r = (001) : \overline{(101)}$	=*	74	143/4	· _	-
$b: m = (0\overline{1}0): (1\overline{1}0)$	=*	<b>58</b>	54	-	
c: a = (001): (100)	=	56	36	56°	351/4'
$a: \varepsilon = (\overline{100}): (\overline{101})$	=	49	10 .	49	10
$a: m = (100): (\overline{110})$	=	31	13	31	6
a:p=(100):(120)	=	50	28	50	202/3
b:p=(010):(120)	=	39	44	<b>3</b> 9	391/3
$c: s = (001): \overline{(102)}$	=	39	11	39	$15^{1}/_{4}$
$s:r=(\overline{102}):\overline{(101)}$	=	35	1	34	591/2
$m \colon r = (\overline{1}  \overline{10}) : (\overline{101})$	=	55	56	55	57
$r:p=(\overline{101}):(\overline{120})$	=	65	19 ·	65	20
a:n=(100):(110)	=	31	16	31	6
n: p = (110): (120)	=	19	12	19	$14^{2}/_{3}$
$b: o = (\overline{010}): (\overline{221})$	=	64	19	64	25 .
$c: \omega = (001) : \overline{(1111)}$	=	77	10	77	71/4
$\omega: m = \overline{(1\overline{1}1)}: \overline{(1\overline{1}0)}$	=	40	58	41	$0^{3}/_{4}$
$\rho: \boldsymbol{b} = (11\overline{2}): (010)$	=	65	32	65	26
$\rho: s = (1\overline{12}): (1\overline{02})$	=	24	28	24	34
$c: t = (001): (\overline{223})$	=	29	59	30	46

Probably cleavable parallel to m.

The salt is appreciably dichroitic: on {100} for vibrations parallel to the orthodiagonal, blood-red; for those parallel to the c-axis, orange; on {010} for the latter direction of vibration, blood-red; for that perpendicular to it, dark blood-red.

On  $\{001\}$  the extinction occurs perpendicularly to the edge: c:a; on m oblique to m:a, and on  $\{010\}$  the angle of extinctions is about  $15^\circ$  with respect to the direction of the c-axis. The optical axial plane is  $\{010\}$ ; inclined dispersion. One axis is visible on  $\{100\}$ .

In solution this substance exhibits a specific rotation for sodium-light of  $+9^{\circ}.24$ ; the rotatory dispersion is only small. After crystallisation the compound appeared to be unchanged; first a small quantity of *iodide* 

was separated, then again the crystals of Fig. 13. If c and r in these crystals be taken as  $\{101\}$  and  $\{\overline{1}01\}$ , with  $a = \{100\}$ ,  $m = \{\overline{1}10\}$ ,  $b = \{0\overline{1}0\}$ , etc., then the parameters may be written as:

$$a:b:c=0,6064:1:0,4596;$$
  
 $\beta=84^{\circ}9'.$ 

Moreover, the forms:  $\varrho = \{11\overline{2}\}$  and  $t = \{2\overline{2}3\}$  were also found with some of these crystals (old coordinates); they occur only as facets, which are scarcely visible.

The rotation in solution appeared to be the same as before, with only feeble rotatory dispersion, - no fission of the complex ion into antipodes evidently having occurred here. The optical activity of the solution. therefore, results merely from the quantity of d-tartaric acid, which is present in the compound in question. Indeed, the iodide prepared from this iodotartrate by precipitation by means of NaI and recrystallisation, appeared to be optically inactive, — its crystalform being completely identical with that of the racemic iodide formerly described. It became evident, that the apparent fission of the complex ion observed in the preliminary experiments needs to be explained wholly by the fission of the admixed triethylene-diamine-salt by the d-tartaric acid, which salt had been formed in the original reaction. Thus e.g. two slightly levogyratory fractions were obtained: one of them  $(a = -9^{\circ}, 20')$  was transformed into the corresponding iodide, and from its solution by slow evaporation flat, badly developed crystals were deposited, which appeared to be no other than those of the rhombic racemic iodide:  $\left\langle Co_3 \frac{(Eine_6)}{(Triam_2)} \right\rangle I_9$ . Predominant

than those of the rhombic racemic iodide:  $\left\{ Co_3 \frac{(Eine_6)}{(Triam_2)} \right\}$  I<sub>9</sub>. Predominant was  $a = \{100\}$ ;  $o = \{111\}$  and  $o' = \{1\overline{1}1\}$  are narrow and about

equally developed; further;  $m = \{110\}$ , also narrow. The crystals were flat and thin, tabular forms parallel to  $\{100\}$  and elongated towards the c-axis. Measured angles:  $(100):(111)=42^{\circ}$  48';  $(100):(1\overline{11})=43^{\circ}$  0';  $\overline{(111)}:(111)==94^{\circ}$  23';  $(100):(110)=33^{\circ}$  8'; etc. The crystals were strongly dichroitic: on  $\{100\}$  for vibrations parallel to the c-axis yellow, for those perpendicular to the former, orange. The plane of the optical axes was  $\{010\}$ , with the a-axis as first bissectrix; the apparent axial angle was only small.

In the same way the so-called iodo-tartrate of  $a=-2^{\circ},50'$ , appeared to be no other than the same rhombic-bisphenoidal racemic iodide in an impure state. The crystals manifested the typical hemihedral form, with  $o'=\{1\overline{11}\}$  much larger than  $o=\{111\}$  and with predominant, large faces of  $a=\{100\}$ , so that they ordinarily appear as oval or lense-shaped individuals, with the forms:  $m=\{110\}$  and  $c=\{001\}$ , very small and  $p=\{410\}$ , besides those already mentioned. The following angles were measured:  $(001):(111)=(001):(1\overline{11})=61^{\circ}13';$   $(110):(111)=(\overline{110}):(\overline{111})=28^{\circ}47';$   $(100):(111)=42^{\circ}48';$  (100):

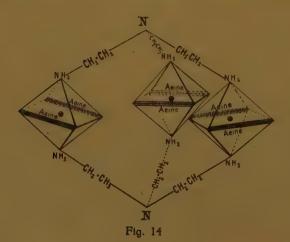
:  $(110) = 33^{\circ} 9'$ ;  $(100) : (410) = 9^{\circ} 15'$ ;  $(111) : (\overline{111}) = 94^{\circ} 24'$ . The parameters are, therefore: a:b:c=0.6529:1:0.9957; the optical properties were the same as already described. In both cases the presence of the also rhombic triethylenediamine-cobaltic iodide and of free d-tartaric acid could, moreover, be demonstrated. As soon, however, as the pure iodotartrate of the threefold complex ion was used in such experiments, no indication of a fission could any more be found.

After all crystals of the salt were deposited and eliminated, the solution of the pure *iodo-tartrate* gave a mother-liquor B, which by slow evaporation gradually got more viscous; from it no or only very small crystals were deposited, but finally it was transformed into an almost resinous mass. This product was solved in water and then, by means of NaI, transformed into the *iodide*. By fractional crystallisation of the solution some fractions of this iodide were separated and investigated with respect to their crystal-forms, as well as to their optical behaviour. It appeared that the first was identical with that of the racemic iodide; moreover, no appreciable rotation of the solutions could be stated.

Endeavours to split the complex ion by means of *d-bromocamphor-sulphonic acid* neither led to any positive result. After the *iodide* was transformed by means of pure *silver-d-bromocamphorsulphonate*, a solution was obtained, which finally yielded a yellow-brownish resinous mass; this could not be obtained in a crystalline form, notwithstanding frequently repeated experiments.

Finally a similar trial was made by means of the *silver*-salt of the optically active *malic acid*. After the AgI was removed, the solution on evaporation on the waterbath only gave a homogeneous mass, from which, even after a long time, no crystals were formed.

In no case even the slightest indication could be obtained of a possible inhomogeneity of the salts formed in the original reaction. It is, therefore, highly probable, that no possibility at all of splitting the inactive salt occurs in this case. The only admittable explanation of this behaviour,



which can be given, is this, that the complex ion involved has really the configuration:  $\begin{bmatrix} B \\ CO \\ Eine_2 \end{pmatrix}_3 = IX$  (see fig. 14 p. 82).

In our opinion, it must, therefore, be considered as a derivative of a trans-compound of the constitution:  $\left\{ Co \begin{array}{c} (E\ddot{\imath}ne)_2 \\ Cl \\ H_2O \end{array} \right\} X_2 \text{ or } \left\{ Co \begin{array}{c} (E\ddot{\imath}ne)_2 \\ Cl_2 \end{array} \right\} X.$ 

Evidently, there must have occurred a shift of the *ethylenediamine*-molecules into their new positions during the reaction. In connection with this conclusion, it is of interest to remark here, that already in many reactions of this kind, such a shift of the substituents round the central atom of the metal has been observed. 1)

For instance: cis-Diaquo-diethylenediamine-cobaltic-chloride, on being heaten with strong hydrochloric acid, appears to yield exclusively the corresponding trans-derivative; in the same way, cis-Rhodanato-diethylene-diamine-cobaltic-chloride gives much more of the trans-, than of the expected cis-derivative; etc. Also in this case the transition of the one class of compounds into the other need therefore not be considered altogether abnormal.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

<sup>1)</sup> A. WERNER, Lieb. Ann. der Chemie, 386, 54, 58, (1912).

Chemistry. — "Equilibria in systems, in which phases separated by a semi-permeable membrane". XIII. By F. A. H. Schreinemakers.

(Communicated at the meeting of November 28, 1925).

The isotonic curves in ternary systems, in which dimixtion into two or three liquids occurs.

Till now we only have discussed the isotonic curves in systems, in which all liquids are mixible with one another in all proportions; we now assume that dimixtion into two or three liquids can occur also.

The sides of the components-triangle are not drawn in order not to enlarge the figure too much; only the angle-point W which represents the diffusing substance W (water or an other component), is indicated. The terminating-points of the isotonic curves, which are indicated in the figure by dotted curves, are situated on the side of the components-triangle, starting from point W.

As known, the region of dimixtion of a ternary system at constant temperature and under a constant pressure, is encircled by the binodal-curve; its points represent conjugated or coexisting liquids, viz. liquids which can be in equilibrium with one another two by two  $^1$ ). Those binodal-curves are represented in the figures by fully drawn curves. The critical points a and  $\beta$  divide the binodal-curve into two branches; with every liquid of the one branch a definite liquid of the other branch can be in equilibrium; some of those conjugated liquids are united in the figures by straight lines, the conjugation-lines. Consequently we find indicated in those figures the equilibria

$$L_{a_1} + L_{a_2}$$
  $L_{b_1} + L_{b_2}$   $L_{c_1} + L_{c_2}$ .

With regard to the extension of the region of dimixtion, we may distinguish two principal cases 2).

A. The region of dimixtion is situated totally within the components-triangle, consequently dimixtion occurs in ternary liquids only, but not in the binary liquids.

B. The region of dimixtion extends itself as far as one of the sides, consequently dimixtion occurs also in one or more of the binary systems. Although the case mentioned sub A experimentally seems to occur as

<sup>1)</sup> For a treatment in detail of ternary equilibria with two and three liquids, compare F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM; Drittes Heft. Zweiter Teil.

<sup>2)</sup> Comp. f.i. the figs. 1-6, l.c.

exception only  $^{1}$ ), yet we will take this as a starting-point at the consideration of the isotonic curves. We may apply viz. the results also to the cases, mentioned sub B, some changes excepted, which occur in the vicinity of the sides of the components-triangle and which we shall indicate further.

In this communication we shall only indicate and describe several properties; in a following communication we shall deduce them with the aid of thermodynamical considerations and we shall enlighten them more in detail.

Let us take two conjugated liquids f.i.  $L_{b_1}$  and  $L_{b_2}$  (figs. 1—3). As both liquids are in equilibrium with one another, they are isotonic with respect to each of the three components, of which they consist. Consequently both liquids have the same O.W.A. (osmotic water-attraction). Therefore, both liquids belong to the same isotonic curve; they are found in fig. 1 on the isotonic curve 5, in fig. 2 on curve 3 and in fig. 3 on curve 4. Of course the same is true for other conjugated liquids.

As regards the position of the point W with respect to the conjugation-lines of the binodal-curve, we can distinguish two cases. In figs. 2 and 3 one conjugation-line viz  $m_1m_2$  goes through the point W; in fig. 1 this is not the case. Further we shall see that this difference has a great' influence on the proceeding of the isotonic curves.

I. None of the conjugation-lines goes through point W (fig. 1).

If we take isotonic curves in the vicinity of the point W, then they are straight lines; at further distance from the point W they are curved (Curve 1 and 2 of fig. 1). Dependent on the increase of the O.W.A. of the liquids of the curves these curves are situated further from the point W and, therefore, they approach more the region of dimixtion till they touch it at last (curve 3). The point of contact coincides with the critical pont  $\alpha$  of the binodal-curve, as we shall see later. Consequently all liquids of curve 3 have the same O.W.A. as the critical liquid  $\alpha$ .

If we take an isotonic curve with still greater O.W.A., f.i. curve 4, then this curve intersects the binodal-curve in the two conjugated points  $a_1$  and  $a_2$ . Then, if we consider stable liquids only, the isotonic curve consists of two branches, separated from one another, united by the conjugation-line  $a_1 a_2$ . As each point of the line  $a_1 a_2$  represents a complex of the two liquids  $a_1$  and  $a_2$ , therefore, each point of this line represents also a complex with the same O.W.A. as that of the liquids of curve 4. If we represent an arbitrary liquid of curve 4 by L, then consequently the osmotic equilibrium

$$L_{\perp}^{\perp}L_{a_1}+L_{a_2} \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

<sup>1)</sup> We find an example in the system: water, phenol and aceton. F. A. H. SCHREINE-MAKERS, Zeitschr. f. Phys. Chem. 33, 84 (1900).

exists, in which equilibrium two liquids occur at one of the sides of the membrane.

An isotonic curve with still greater O.W.A., f.i. curve 5 (fig. 1), intersects the binodal-curve in the conjugated points  $b_1$  and  $b_2$ ; curve 6

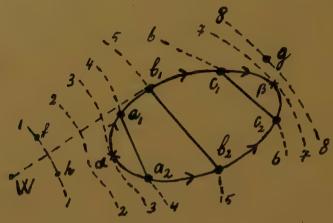


Fig. 1.

intersects them in the points  $c_1$  and  $c_2$  etc. At last we get again, as is represented by curve 7, an isotonic curve, touching the binodal-curve; this point of contact coincides with the critical point  $\beta$ . Isotonic curves with still greater O.W.A., f.i. curve 8, are situated again totally outside the field of dimixtion.

Hence follows that the O.W.A. of the liquids of the binodal-curve increases on each of the two branches in the direction of the arrows viz. from the critical point  $\alpha$  towards the critical point  $\beta$ . Consequently the O.W.A. of the liquids of the binodal-curve is a minimum for the critical liquid  $\alpha$  and a maximum for the critical liquid  $\beta$ .

The conjugation-line  $b_1$   $b_2$  divides fig. 1 into two parts; in the one part is situated the point W. If we start from the point  $b_1$  along the binodal-curve towards that part of the plane, in which point W is situated (consequently from  $b_1$  towards a), then we shall say that we go along the binodal-curve towards point W. If, however, we go from  $b_1$  along the binodal-curve towards the other part of the plane (consequently from  $b_1$  towards the point  $\beta$ ), then we shall say that we move away from the point W along the binodal-curve.

Consequently we move away along the binodal-curve from point W, if we proceed along this curve:

in fig. 1 starting from  $\alpha$  towards  $\beta$ ;

in fig. 2 starting from the points  $m_1$  and  $m_2$  towards  $\alpha$  and  $\beta$ ;

in fig. 3 starting from the points  $\alpha$  and  $\beta$  towards  $m_1$  and  $m_2$ ; those directions are indicated in the figure by arrows.

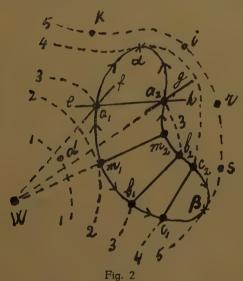
In a following communication we shall deduce the property:

the O.W.A. of the liquids of a binodal-curve increases in that direction, in which we move away from the point W along the binodalcurve.

If we apply this to fig. 1 then we find, in accordance with above, that the O.W.A. must increase along the binodal-curve in the direction of the arrows, viz. from  $\alpha$  towards  $\beta$ .

II. One of the conjugation-lines goes through point W (figs. 2 and 3). In the figs. 2 and 3 the binodal-curves are drawn in such a way that the conjugation-line  $m_1 m_2$  goes through the point W. In order to indicate more easily the proceeding of the isotonic curves, we have given to the binodal-curves another form than in fig. 1; this has no influence on the results of the considerations. We now distinguish the two cases, represented by the figures 2 and 3.

A. If we go in fig. 2 along the binodal-curve in the direction of the arrows, therefore, from  $m_1$  or  $m_2$  towards  $\alpha$  or  $\beta$ , then we move away from the point W. In accordance with the rule, mentioned above, on the change of the O.W.A. of the liquids of a binodal-curve, the O.W.A.



must increase, therefore, in the direction of the arrows; consequently it is a minimum for the liquids  $m_1$  and  $m_2$  and a maximum for the critical liquids  $\alpha$  and  $\beta$ .

The isotonic curve 1 is situated in fig. 2 totally outside the region of dimixtion; dependent on the increase of the O. W. A., they approach this region till they touch it at last (curve 2). It now follows from the above. which we shall deduce later also in another way, that this point of contact coincides with  $m_1$ . As liquid  $m_2$  has the same O. W. A. as  $m_1$  and consequently also as all liquids of curve 2, the

isotonic curve (if we consider stable states only) consists of a curve and the isolated point  $m_2$  which is united with  $m_1$  by a conjugation-line. Consequently an osmotic equilibrium:

$$L_{\perp}^{\perp}L_{m_1}+L_{m_2}$$
 . . . . . . . . (2)

can exist, in which L represents an arbitrary liquid of curve 2.

Isotonic curves with larger O.W.A. consist of three branches, separated from one another. If we take f.i. curve 3 (fig. 2) then those branches are united by the conjugation-lines  $a_1 \ a_2$  and  $b_1 \ b_2$ . The systems  $L_{a_1} + L_{a_2}$ 

and  $L_{b_1} + L_{b_2}$  have the same O.W.A. as all liquids of curve 3; we may have, therefore the osmotic equilibria:

$$L_{1}^{\dagger}L_{a_{1}}+L_{a_{2}}$$
  $L_{1}^{\dagger}L_{b_{1}}+L_{b_{2}}$   $L_{a_{1}}+L_{a_{2}}^{\dagger}L_{b_{1}}+L_{b_{2}}$ . (3)

in which L represents an arbitrary liquid of curve 3. In the last one of those equilibria two liquids occur on both sides of the membrane.

Isotonic curves with larger O.W.A. approach more the points  $\alpha$  and  $\beta$ . If we assume that the O.W.A. of the critical liquid  $\alpha$  is smaller than that of the critical liquid  $\beta$ , then we can represent the isotonic curve, going through point  $\alpha$ , by curve 4. This curve touches the binodal-curve in  $\alpha$  and intersects it in the points  $c_1$  and  $c_2$ . Consequently we now may have an osmotic equilibrium:

in which at the one side of the membrane a critical liquid and at the other side two liquids.

An isotonic curve with the same O.W.A. as liquid  $\beta$  touches the binodal-curve in  $\beta$  (curve 5) and is situated further totally outside the region of dimixtion.

B. In order to proceed in fig. 3 along the binodal-curve in such a way that we move away from the point W, we have to go in the direction of the arrows, viz. starting from a and  $\beta$  towards  $m_1$  and  $m_2$ . Conse-



quently the O.W.A. of the liquids must increase also in the direction of the arrows; it is a minimum, therefore, in the critical points and a maximum in  $m_1$  and  $m_2$ .

The isotonic curve 1 is situated in fig. 3 still totally outside the region of dimixtion; curves with larger O.W.A. approach this region, in order to touch it at last. Of course the point of contact must be a liquid, the O.W.A. of which is a minimum, therefore one of the critical liquids  $\alpha$  or  $\beta$ . If the O.W.A. of  $\beta$  is smaller than that of  $\alpha$ , then we may represent the isotonic

curve by curve 2. The isotonic curve with an O.W.A. equal to that of the liquid a is represented by curve 3; isotonic curves with still greater O.W.A. (as f.i. curve 4) consist of three parts, separated from one another, united with one another by two conjugation-lines  $(a_1 \ a_2 \ and \ b_1 \ b_2)$ .

The isotonic curve with an O.W.A. equal to that of the liquid  $m_1$  is represented by curve 5, which touches the binodal-curve in  $m_1$ , and the isolated point  $m_2$ .

The osmotic equilibria, mentioned above sub (2) and (3) can occur also now; then in (2) L represents a liquid of curve 5 (fig. 3) and in (3) a liquid of curve 4 (fig. 3).

We can briefly summarize the previous considerations.

I. The O.W.A. of the liquids of a binodal-curve increases in that direction in which we move away from the point W.

Hence follows:

II. None of the conjugation-lines of the binodal-curve goes through the point W (fig. 1).

The O.W.A. of the liquids of the binodal-curve is a minimum in the one — and a maximum in the other critical point.

III. One of the conjugation-lines goes through point W (figs. 2 and 3).

A. The O.W.A. of the liquids of the binodal-curve is a minimum in the points, situated on the conjugation-line going through W and a maximum in the critical points (fig. 2).

B. The O.W.A. of the liquids of the binodal-curve is a minimum in the critical points and a maximum in the points, situated on the conjugation-line going through point W (fig. 3).

IV. In each of the critical points and in the points which are situated on the conjugation-lines going through point W, an isotonic curve touches the binodal-curve. Consequently we find in fig. 1 two isotonic curves touching the binodal-curve and in figs. 2 and 3 three of such curves.

If the region of dimixtion extends itself as far as into one or two of the sides of the components-triangle, then in the figures one or both critical points disappear. With the aid of the above-mentioned properties I—IV, of which we may apply always I, yet we can project then the schematical diagrams and define the direction in which increases the O.W.A. of the liquids along the binodal-curve.

However, the following is to be observed with respect to the conjugation-lines going through the point W. The conjugation-lines of the figs. 1—3 unite ternary liquids; for this reason we call them ternary conjugation-lines. If, however, the binary curve terminates in the points  $p_1$  and  $p_2$  on one of the sides of the components-triangle, then  $p_1$   $p_2$  is a binary conjugation-line, which always goes through the point W. The property, mentioned in IV, that in the points, which are situated on a conjugation-line, going through point W, an isotonic curve touches the binodal-curve, is true only for ternary conjugation-lines  $(m_1m_2)$  in figs. 2 and 3), but not for binary ones. In the latter case the common point viz. is not a point of contact, but a point of intersection. We shall refer to this at the discussion of the special cases.

We have drawn the isotonic curves 4, 5 and 6 in fig. 1, as if they terminate in the region of dimixtion; this is, however, not the case. If we take f.i. curve 4, then this does not finish in  $a_1$  and  $a_2$ , but it goes through the region of dimixtion from  $a_1$  towards  $a_2$ ; this part, situated within the region of dimixtion, however, represents only metastable and unstable liquids, which, however, have all the same O.W.A. as the other liquids of curve 4. If, however, we limit ourselves, as we have done above, to stable states, then the isotonic curve consists of two separated branches, united by the conjugation-line  $a_1$   $a_2$ .

Of course the same is valid for the isotonic curves of the other figures. If we take f.i. curve 3 of fig. 2, then this does not terminate in  $a_1$  and  $a_2$  and in  $b_1$  and  $b_2$ . We now may distinguish two cases:

- 1. Curve 3 consists of a single continuous curve, which passes through the region of dimixtion from  $a_1$  towards  $a_2$  and from  $b_2$  towards  $b_1$ .
- 2. Curve 3 consists of two separated parts. The branch coming in  $a_1$  passes viz. through the region of dimixtion from  $a_1$  towards  $b_1$ . The other branch, on which are situated the points  $a_2$  and  $b_2$ , forms a closed curve, which is situated partly outside and partly within the region of dimixtion. In a following communication we will discuss a single case more in detail. 1)

In communication III we have discussed the property:

the saturation-curve of a solid substance and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or within the supplement-angle. If the saturation-curve touches one of the legs of this angle, then the isotonic curve touches the other leg.

As we will show later, for the equilibria treated now, is valid:

the binodal-curve and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. If the binodal-curve touches one of the legs of that angle, then the isotonic curve touches the other leg.

Let us take in fig. 2 the point of intersection  $a_1$ . As liquid  $a_1$  can be in equilibrium with liquid  $a_2$ , and as the diffusing substance is represented by point W, angle  $Wa_1a_2$  (and its opposite-angle  $ea_1f$ ) is the conjugation-angle in  $a_1$ . As the binodal-curve is situated in the vicinity of  $a_1$  within the conjugation-angle, curve 3 must be situated also within this angle.

<sup>1)</sup> In order to imagine oneself properly the position of this curve, compare F. A. H. Schreinemakers, Die heterogenen Gleichgewichte von Bakhuis Rooseboom. Drittes Heft, Zweiter Teil. Fig. 135—139 pg. 330—332. In those figures a part of the binodal-curve is drawn, recognizable by its conjugation-lines. If we imagine the diffusing substance to be represented by point V, then the curve, indicated by the figures I, II and III, can represent an isotonic curve. The dotted parts of this curve represent the metastable and unstable states.

In point  $a_2$  (fig. 2) angle  $Wa_2a_1$  (and its opposite angle  $ga_2h$ ) is the conjugation-angle; the two other angles (viz.  $a_1a_2g$  and  $Wa_2h$ ) form, therefore, the supplement-angle. As the binodal-curve is situated in the vicinity of  $a_2$  within the supplement-angle, curve 3 must be situated also within this angle.

In fig. 1 a tangent is drawn from W, which touches the binodal-curve in  $b_1$ . As the binodal-curve touches, therefore, the leg  $b_1$  W of the conjugation-angle, curve 5 must touch in  $b_1$  the other leg, viz. the conjugation-line  $b_1$   $b_2$ .

From the property above-mentioned of binodal-curve, isotonic curve and conjugation-angle follows:

An isotonic curve, which touches the binodal-curve in a critical point, is curved in the same direction as the binodal-curve in the vicinity of this point.

This is seen in fig. 1 with the curves 3 and 7; in fig. 2 with the curves 4 and 5; in fig. 3 with the curves 2 and 3. Of course this will be still also the case with isotonic curves, which are situated on some distance of the critical points, as f.i. with curve 2 in fig. 1, etc.

We imagine two conjugated liquids  $q_1$  and  $q_2$ . We unite the points  $q_1$  and  $q_2$  with the point W, which represents the diffusing substance, so that the angle  $q_1$   $Wq_2$  arises. If we limit ourselves to stable states, then from each of the points  $q_1$  and  $q_2$  a branch of the isotonic curve starts. We now can show:

the stable branches of an isotonic W-curve, starting from two conjugated points  $q_1$  en  $q_2$ , are situated always outside the region of the angle  $q_1 W q_2$ .

If we take f.i. the points  $a_1$  and  $a_2$  (fig. 1—3) then we see that the branches starting from those points, are situated outside the region of the angle  $a_1$   $Wa_2$ . The same is valid in points  $b_1$  and  $b_2$ ,  $c_1$  and  $c_2$ , etc.

With the aid of those and other properties discussed above, we are able to deduce already at once schematically the position and proceeding of the isotonic curves, if the position of the binodal-curve and its conjugation-lines is known.

Of the many phenomena, which may occur in osmotic systems with a region of dimixtion, we only will discuss some briefly. Let us take f.i. the osmotic system:

$$L_a \xrightarrow{} L$$
 fig. 2 . . . . . . . (5)

in which L represents a liquid of the isotonic curve 5. Consequently L has a greater O.W.A, than  $L_d$ , so that the water diffuses in the direction of the arrow viz. from  $L_d$  towards L. We now assume that the quantities of  $L_d$  and L are taken in such a way that an osmotic equilibrium of curve 3 arises. As the line Wd intersects the line  $a_1$   $a_2$  viz. the conjugation-line of the isotonic curve 3,  $L_d$  passes, therefore into a

complex of the liquids  $a_1$  and  $a_2$ . It depends on its position on curve 5, which shall arise from liquid L. If L represents the liquid K, then (5) passes into the osmotic equilibrium:

$$L_{a_1} + L_{a_2} \mid L'_K$$
 fig. 2 . . . . . . (6)

in which  $L'_K$  is represented by the point of intersection of the line WK with curve 3. If we take in (5) for L the liquid i, then arises

$$L_{a_1} + L_{a_2} \mid L_{a_1} + L_{a_2} \cdot \ldots \cdot \ldots \cdot (7)$$

therefore, an osmotic system, in which appear the same liquids at both sides of the membrane. If we take in (5) for L the liquid r, then arises the osmotic equilibrium:

in which  $L'_r$  is represented by the point of intersection of the line Wr with the branch of curve 3, situated between  $a_2$  and  $b_2$ . If we take in (5) for L the liquid s or the critical liquid  $\beta$ , then arises the osmotic equilibrium:

in which two liquids are found on both sides of the membrane.

In following communications we shall discuss more in detail the phenomena, occurring on the similar osmotic equilibria setting in.

(To be continued).

Physiology. — "The Balance in Radio-physiological Equilibria shifted by l. adrenalin towards the Alpha-side, and by d. adrenalin towards the Beta-side." By Prof. H. ZWAARDEMAKER.

(Communicated at the meeting of October 31, 1925).

The micro-radioactivity of animal tissues, which is of the order of the radio-activity of some medicinal springs, but is of totally different origin, depends almost exclusively on the presence of the element potassium in the cells. This potassium can be washed out, and if this is done, it appears that a number of functions are arrested, which can be restored again, when an amount of either potassium or another radioactive element is added, sufficient to render it approximately radio-equivalent to the previous radioactivity 1). As substituting elements we found thus far: Rb, Th, U, Io, Ra, Em (Radon) 2).

When the microradioactivities alluded to are combined in physical experiments, a summation of their actions takes place (ionisation, photographic effect), but when this takes place in a biological system, such a summation does not always occur. It then appears that two groups must be distinguished: the first group consisting of the elements K and Rb, which have the property of emitting beta-rays, and the second consisting of the elements Th, U, Io, Ra, Em (Radon), which have the property of emitting chiefly alpha-rays. When an element of one group is taken up in the perfusing fluid that contains an element of the other group, their effects will counteract each other (physiological antagonism). In the latter case we may by carefully weighing the two actions approximate an equilibrium in which the function is suspended, just as it is arrested when the original potassium has been sufficiently washed out. Such an equilibrium we will call a radiophysiological equilibrium <sup>3</sup>.

It stands to reason that a radiophysiological equilibrium may be disturbed by enlarging or lessening the quantity of one of the counterbalancing elements. The disturbance will, however, also occur, when the sensitivity of the organ is modified, and this modification is made different for alphaand beta-rays. This can be effected by means of a sensitizer 4).

Among the sensitizers one of the strongest is the natural l. adrenalin 5), which being prepared in the cells of the medulla of the suprarenal capsule,

<sup>1)</sup> These Proceedings 19 p. 633.

<sup>2)</sup> Erg. d. Physiol. Bd. 19, S. 326, (1921).

<sup>3)</sup> These Proceedings 19 p. 1043.

<sup>4)</sup> These Proceedings 20 p. 768.

<sup>5)</sup> These Proceedings 23 p. 838.

is transmitted by the blood to the organs. Special addition of this l. adrenalin to the perfusing liquid, which has brought an organ (generally the heart of a cold-blooded animal) to a radiophysiological equilibrium, restores the normal function. Experiments, conducted advisedly, proved this te be due to a shifting of the balance to the side of the alpha-element, which, owing to the sensitizer has obtained predominance. It has likewise been proved that the old equilibrium can be restored by superaddition of some more of the beta-element.

Considerations, which I need not go into here, induced me also to try the synthetic d. adrenalin. (The Farbestoff-fabrike, late MEISTER, LUCIUS and Bruning at Höchst kindly furnished a preparation of d. suprarenin). It was remarkable that in experiments on the hearts of frogs and eels in equilibria between 175 mgr KCl and 15 mgr Uranylnitrate, between 300 mgr KCl and 29 mgr Uranylnitrate, between 500 mgr KCl and 40 mgr Uranylnitrate, etc. d. adrenalin turned the radiophysiological balance towards the beta-element, so that a superaddition of alpha-element was required to return to the old equilibrium. The dosage of d. adrenalin required was 1:1000000 1). This was established in half a dozen cases. I purpose to continue my observations later on. For the present I have utilized the small supply of d. adrenalin (d. suprarenin) for observations of another character, in order to find an explanation for the remarkable phenomenon. This phenomenon is so very peculiar because thus far only a quantitative functional difference between 1.- and d. suprarenin has been brought to light. A qualitative difference in their behaviour I presume to have found here for the first time.

In addition this new experience may encourage us to penetrate more deeply into the process of sensibilization for corpuscular radiation, varying with alpha- and beta-radiation.

Meanwhile our preliminary experiments have already borne out that the problem under consideration is extremely complicated. It can only be solved when we dispose of larger amounts of suprarenin. Such a larger amount is all the more necessary as it may very well be possible that the originally dextrorotatory preparation, which possesses great optic activity, might, if the solution is kept for some time, contain some of the far more active levorotatory adrenalin 2), without our being able to observe this in the circumpolarisator on account of the discolouration. The complications thereby ensuing can only be unravelled when more synthetic chemicals are at our disposition.

<sup>&</sup>lt;sup>1)</sup> In order to return to the old equilibrium we used in the second equilibrium 10 mgr. Uranylnitrate, i.e.  $25\,^{0}/_{0}$  of the original amount. This is the minimal amount required for the shifting.

<sup>2)</sup> F. M. JAEGER, Lect. on the principle of symmetry. Sec. ed. Amsterdam 1920, p. 232.

Physics. — "On the Equation of State of Solid Substances (Metals) in connection with their Compressibility and with the Pressure and Temperature Coefficient of this Quantity." By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of December 19, 1925).

I.

# The Equation of State.

1. It is known that VAN DER WAALS's equation of state

holds for gases and liquids at higher temperatures. This equation may be imagined as having arisen from the Virial-equation (everything still to be multiplied by  $\frac{3}{2}$ )

$$pv + \frac{a}{v} - \frac{b}{v-b}RT = RT, \quad . \quad . \quad . \quad . \quad (2)$$

in which pv is the virial of the external forces (pressure),  $\frac{a}{v}$  the so-called virial of attraction and  $-\frac{b}{v-b}RT$  the virial of repulsion, which latter is proportional to RT, i.e. to the vis viva  $L=\frac{3}{2}RT$  of the progressive motion of the molecules. Consequently it is immaterial for the equation of state whether the molecules contain only one or more atoms, as RT always refers to L, and not to L + the energy of the atoms in the molecule.

In most cases the temperature functions of the quantities a and b, which about compensate each other, and also the small volume-function of a, may be neglected here. But this may by no means be done with the very strong dependence on the volume of b, which may be represented by the simple equation 1)

$$b = \frac{b_g}{1 + \frac{b_g - b_0}{v}}, \text{ or } v - b_0 = (v - b)\left(1 + \frac{b_g - b_0}{v}\right).$$
 (3)

The second of equations (3) can be derived from the first by calculating v-b from it. Then the virial equation (2) becomes:

<sup>1)</sup> Compare my book: "die Zustandsgleichung von Gasen und Flüssigkeiten", Leipzig, L. Voss, 1924, especially p. 74—79 and 91. Also Z. f. anorg. u. allg. Ch. 140, 58—60 (1924).

$$pv + \frac{a}{v} - RT \frac{b_g}{v - b_0} = RT, \dots$$
 (2a)

and the equation of state (1), ensuing from it, becomes:

$$p + \frac{a}{v^2} = \frac{RT}{v - b_0} \left( 1 + \frac{b_g - b_0}{v} \right) \dots$$
 (14)

That the above equation for the dependence on the volume of b renders all the thermal quantities (compressibility, expansibility etc.) for liquids with great accuracy, I have shown before already more than once  $^1$ ). If e.g. the quantity  $1+(b_g-b_0):v$  is neglected, values 4 or 5 times too small are e.g. obtained for the coefficient of compressibility.

As for ordinary substances ( $\gamma=0.9$  to 1) the value  $b_g:b_0$  lies in the neighbourhood of 3,8 to 4,8 at  $T=\frac{1}{2}$   $T_k$ ,  $(b_g-b_0):b_0$  will be 2,8 to 3,8, and  $(b_g-b_0):v$  will be =2,14 to 2,85, because v is =1,31 to 1,33  $b_0$  at temperatures in the neighbourhood of the solidifying point (T about  $=\frac{1}{2}$   $T_k$ ) <sup>2</sup>). Thus 2,5 is e.g. found for  $(b_g-b_0):v$  for mercury, 2,0 for  $C_2H_5Cl$ , 1,8 for ether, 2,0 for molten copper (see IV) <sup>3</sup>). Here T is, however, higher than 1/2  $T_k$  for ether and ethylchloride, hence  $a_t:a_k$  is <1,5, whereas mercury and molten copper belong strictly speaking to another category.

For the important quantity  $\frac{v}{v-b}$  the following equation is found, when the external pressure is negligible by the side of  $\frac{a}{v^2}$ :

$$\frac{v}{v-b} = \frac{a/v}{RT} = \frac{fRT_k}{RT} = \frac{f}{m},$$

in which f is the known vapour pressure factor (still slightly variable with the temperature). For ordinary substances the value of 14 to 16 is found for  $\frac{v}{v-b}$  at  $m=\frac{1}{2}$  and with f=8  $\gamma=7$  to 8. We may, therefore,

$$\begin{split} &\frac{(b_g)_t}{b_0} = \frac{(b_g)_t}{(b_g)_k} \times \frac{(b_g)_k}{b_k} \times \frac{b_k}{b_0} = (1.5 \text{ à } 1.6) \times (\gamma + \frac{1}{2}) \times 2\gamma = (1.5 \text{ to } 1.6) \ \gamma \ (2\gamma + 1), \\ &\text{as at } T = \frac{1}{2} \ T_k \ \frac{(b_g)_t}{(b_g)_k} = \frac{a_t}{a_k} = 1.5 \text{ to } 1.6. \text{ Further from } d = d_0 - 2\gamma m \text{ follows} \\ &\frac{d}{d_0} = \frac{v}{v_0} = 1 - \frac{\gamma}{1+\gamma} m, \text{ as } d_0 \text{ is } = 2 \ (1+\gamma). \text{ Hence with } \frac{T}{T_k} = \frac{1}{2} \text{ we get} \\ &\frac{v}{v_0} = \frac{v}{b_0} = \frac{2 \ (1+\gamma)}{2+\gamma}. \end{split}$$

<sup>1)</sup> Compare inter alia pages 108-121 of the cited book.

<sup>&</sup>lt;sup>2</sup>) Compare also Z. f. anorg. u. allg. Ch. 149, 349—350 (1925). At a temperature T the following relations are valid:

<sup>&</sup>lt;sup>3</sup>) Compare also Z. Gl. p. 114-115 and 156-162.

write for "ordinary" liquids in the neighbourhood of the solidifying point:

$$\frac{v}{v-b} - 15$$
;  $\frac{b_g - b_0}{v} = \frac{\varphi}{v} = \omega - 2.5$ . (liquid,  $m = \frac{1}{2}$ ).

# 2. For solid substances the equation of state

$$p + \frac{a}{v^2} - \frac{b}{v^n} = \gamma \frac{RT}{v}$$

has often been proposed (GRÜNEISEN and others), in which at very low temperatures  $PT^4$  must be substituted for RT, in accordance with the expression for the Energy holding then. Here P is a volume function, which is still to be determined. It is, however, not equal to the coefficient of  $T^4$  in the expression for E at very low temperatures.

But this equation cannot possibly be correct. For at very high pressures the first member would then approach to  $\infty$  at a given temperature, whereas the second member remained finite. Hence here too v-b must necessarily occur in the equation of state, and not  $v^n$ .

This is, however, not all. If the coefficient  $\gamma$  occurring in the above equation is calculated theoretically,  $\frac{1}{3} \gamma = (3n+5):6$  is found for it 1) (and not (3n-1):6, as Grüneisen erroneously gives). But since for  $\frac{1}{3} \gamma$  in different metals values are experimentally found between  $\frac{4}{3}$  and  $\frac{9}{3}$  (average 2; see II § 2), n would lie between 1 and 4, which is impossible. For in the first place n cannot be = 2, which would yet be the case with many metals; secondly it is inconceivable that in the term  $b:v^n$ , referring to the repulsive forces, the exponent of v should be different for every metal; and thirdly fractional exponents would frequently occur.

All these considerations completely condemn the equation of state in question. If on the contrary

is written for solid substances at higher (i.e. at ordinary) temperatures, in which equation b is again a function of v, represented by a relation analogous to (3), all the discrepancies disappear, and also the discontinuity between the form of the virial of repulsion in liquids and that in solid bodies which is difficult to understand. At bottom it will, indeed, be pretty well immaterial whether the molecules move — as in liquids — along curvilinear "open" paths between the other molecules, frequently "colliding" (which may also take place "at a distance"; it is not neces-

<sup>1)</sup> Compare my earlier Paper in These Proceedings 27, 902—904 (1924).

sary that the molecules exactly touch 1), or — as in solid substances — move in curvilinear "closed" paths round a certain state of equilibrium, without shifting from one molecule to another. This with reference to the so-called "dynamic" virial of repulsion, which accordingly, as in liquids in equation (2), keeps the form  $-\frac{b}{v-b}RT$ ; this, added to RT in the second member, again yielding  $\frac{RT}{v-b}$  after division by v.

But what distinguishes solid bodies from liquids (and gases), is that in consequence of the fact that the molecules are bound to definite positions of equilibrium, there must necessarily a term  $\lambda$  be present in the equation of state, which refers to the so-called "static" virial of repulsion. Hence this, no more than the static virial of attraction a/v, will contain the temperature as a factor, but it will, of course, contain v-b in the denominator, as otherwise at T=0,  $p=\infty$  equation (4) would lead to an absurdity.

Accordingly the virial equation has now the following form (everything still to be multiplied by 3/2):

$$pv + \left(\frac{a}{v} - \lambda \frac{v}{v - b}\right) - \frac{b}{v - b}RT = RT.$$

Here too, in the case of solid substances, it is quite indifferent whether the molecules are mon-atomic or pluri-atomic, because in both members RT refers again to the progressive energy of the molecules, now in closed paths (so that L is half the total energy of the path) instead of in open paths, as with liquids and gases.

In what follows we shall show that the equation (4), combined with a relation b = f(v) of the form (3), represents the experimental results for metals perfectly accurately in every respect — not only the coefficient of compressibility and expansibility, but also the coefficients of pressure and temperature of the first-mentioned coefficient, which the earlier theories of GRÜNEISEN and others were entirely inadequate to do.

#### II.

# Closer Consideration at Higher temperatures.

1. The quantity  $\lambda$ , occurring in the above equation (4), can be expressed in the volume  $v_0$ , which the metal occupies at T=0 ( $PT^4$  is then substituted for RT), when the external pressure p=0 is retained, i. e. when the

<sup>1)</sup> In this we think e.g. of the molten electrolytes, where the molecules can remain at comparatively large distances apart from each other. Compare These Proceedings 28, 789—793 (1925), and also Z. f. anorg. u. allg. Ch. 149, 337—344 (1925), where we found about 2,7 for the ratio between the diameter of the molecules and the longitudinal dimension of the elementary cubes.

solid substance, as usually, is not under "strain". Then  $\frac{a}{v_0^2} = \frac{\lambda}{v_0 - b_0}$ , is obtained, hence  $\lambda = \frac{a}{v_0^2} (v_0 - b_0)$ .

In this  $b_0$  is the value of b corresponding with  $v_0$ , according to the equation

$$b = \frac{b_g}{1 + \frac{b_g - b_{00}}{v}}$$
 or  $v - b_{00} = (v - b) \left(1 + \frac{b_g - b_{00}}{v}\right)$ 

which corresponds to (3), or also, when we write  $b_g - b_{00}$  for abbreviation  $= \varphi$ :

$$b = \frac{b_g}{1 + \frac{\varphi}{|v|}}, \text{ or } v - b_{00} = (v - b)\left(1 + \frac{\varphi}{v}\right), \dots$$
 (5)

from which then follows  $b_0=b_g:\left(1+\frac{\varphi}{v_0}\right)$ . In this equation (5)  $b_g$  is evidently again the (fictitious) value of b, when v should be  $=\infty$ . The other limiting value  $b_{00}=v_{00}$  is evidently the value of b, when in (5) we take  $p=\infty$ . This is, therefore, the smallest volume possible, that the solid substance can occupy at the utmost compression. Hence we distinguish two limiting volumes with the corresponding values of b, viz.  $v_0$  and  $b_0 < v_0$  at T=0, p=0, and  $v_{00}=b_{00}$  at  $p=\infty$ .

The quantity  $\frac{\varphi}{v}$  is much smaller in solid substances than in liquids, viz. = 0,6 in solid copper as we shall see in IV, as against an average value of 2,5 in ordinary substances  $\left(m = \frac{1}{2}\right)$ , so that the variability of b is by no means so great.

**2.** The quantity  $\frac{v}{v-b}$ . From the equation of state (5) follows immediately:

$$s = \left(\frac{dp}{dt}\right)_{\parallel} = \frac{R}{v - b} = \frac{R}{v} \times \frac{v}{v - b},$$

and as the coefficient of tension s according to a known identity is  $=-\left(\frac{dv}{dt}\right)_p:\left(\frac{dv}{dp}\right)_t$ , we may also write  $s=\frac{a}{\sigma}$ , in which  $a=\frac{1}{v}\left(\frac{dv}{dt}\right)_p$  is the coefficient of expansion, and  $\sigma=-\frac{1}{v}\left(\frac{dv}{dp}\right)_t$  is the coefficient of compressibility. Hence  $\frac{a}{\sigma}=\frac{R}{v}\times\frac{v}{v-b}$ , i.e.

$$\frac{v}{v-b} = \frac{a}{\sigma} \times \frac{v}{R}, \qquad (6)$$

from which the ratio v:(v-b) can be calculated for every solid substance, when  $\alpha$  and  $\sigma$  are known. Thus e.g. in copper at  $20^{\circ}$ C  $\alpha=3\times17.10^{-4}$ ,  $\sigma=0.73.10^{-12}$  (p in dynes per cm<sup>2</sup>), v=63.57:8.933=7.116, and  $R=83.17.10^{6}$  in ergs. Hence:

$$\frac{v}{v-b} = \frac{51 \cdot 10^{-6}}{0.73 \cdot 10^{-12}} \cdot \frac{7,116}{83,17 \cdot 10^{6}} = \frac{362,9}{60,7} = 5,98,$$

so that (see for  $\frac{\varphi}{v} = \omega$  Chapter IV)

$$\frac{v}{v-b} = 6$$
;  $\frac{b_g - b_{00}}{v} = \frac{\varphi}{v} = \omega = 0.6$  (solid copper 20°C.)

may be put. For other metals the following values are found in exactly the same way:

Cu Ag Au | Mg | Zn Cd | Al | Sn Pb | Ta | Bi | W | Fe Ni Pd Pt 6 7 9 | 5 | 
$$\pm 7 \pm 9$$
 | 6 | 7 8 | 5 |  $\pm 4$  | 4 | 5 5 7 7, mean about 6.

If in (4)  $\frac{2}{3}L$  is substituted for  $RT^{-1}$ ), then  $\frac{2}{3}c'_{v}$  is to be substituted for R, in which  $c'_{v}$  represents the specific heat referring to the pure progressive energy (= half the total energy of path) of the molecule (atom) at constant volume. We then get:

$$\frac{a}{\sigma} = \frac{2|_3 c'_v}{v - b},$$

from which it therefore follows, that as v-b does not approach 0 at T=0 and p=0, but approaches the *finite* value  $v_0-b_0$  (see above), and also  $\sigma$  remaining *finite*, the coefficient of expansion  $\alpha$  will always run parallel with  $c'_v$ , and will, therefore, also approach 0 at very low temperatures, where  $c'_v$  approaches 0; and this about proportional to  $T^4$ . In this way this property of  $\alpha$  is proved in an independent way, and *not* in the way indicated by NERNST and others on the ground of perfectly wrong formulae. (compare my Paper in These Proc. 27, 911—913 (1924) already cited).

According to the earlier equation of state  $p+\frac{a}{v^2}-\frac{b}{v^n}=\gamma\frac{RT}{v}$ ,  $\gamma\frac{R}{v}$  would have been found for  $\left(\frac{dp}{dt}\right)_v=\frac{a}{\sigma}$ , instead of  $\frac{R}{v}\times\frac{v}{v-b}$ . It is seen from this that the earlier  $\gamma$  (determined by  $\frac{1}{3}\gamma=\frac{3n+5}{6}$ ) is nothing else than the ratio  $\frac{v}{v-b}$  in the new equation of state. And it is very plausible that

<sup>1)</sup> This is not perfectly correct. We shall see later on that there is a difference. At higher temperatures this difference approaches, however, to 0, but at very low temperaratures P and A are not equal to each other in  $L = AT^4$ , and  $PT^4$  in the equation of state.

this ratio will assume different values at e.g.  $20^{\circ}$  according to circumstances (different values of a and of  $T:T_k$ , etc.), whereas the older equation of state would lead to great absurdities with regard to n (see I).

As regards the quantity  $\lambda$  in the equation of state (4), it follows immediately from  $\lambda = \frac{a}{v_0^2} (v_0 - b_0) = \frac{a}{v_0} \frac{v_0 - b_0}{v_0}$ , that  $\lambda$  is about  $= \frac{1}{6} \frac{a}{v_0}$ , as  $\frac{v_0 - b_0}{v_0}$  will hardly differ from  $\frac{v - b}{v} = \frac{1}{6}$ . If we assume that  $\frac{a}{v_0}$  (solid) is practically  $= \frac{a}{v_0}$  (liquid), which is quite fulfilled with respect to a as we shall see soon, and with great approximation with respect to  $v_0$ , then  $\frac{a}{v_0} = 7\gamma \cdot RT_k$  will follow from  $RT_k = \frac{2}{7} \frac{a}{b_k} = \frac{1}{7\gamma} \frac{a}{b_0}$  (liquid), because  $b_k = 2\gamma \cdot b_0$  and  $b_0 = v_0$  ( $\gamma$  is here the coefficient of direction of the straight joining line between  $d_k$  and  $\frac{1}{2} d_0$ ). Now  $\gamma$  is = 1.76 for copper 1) according to our formula  $2\gamma = 1 + 0.038 \sqrt{T_k}$ , with  $T_k = \text{about } 4400^\circ$ ; hence  $\frac{a}{v_0} = 12.3 RT_k$  and  $\lambda = 2 RT_k$ . We have therefore (for copper):

$$\lambda - \frac{1}{6} \frac{a}{v_0}$$
, or  $-2RT_k$ .

3. We shall now calculate the different values of v and b, both for solid and (by way of comparison) for liquid copper. For solid copper at  $20^{\circ}$  C. we found already above v=63.57:8,933, i.e.  $v_{20}=7,116$ . From this the value  $v_0=7,046$  is easily calculated at T=0, p=0. For the coefficient of expansion between  $16^{\circ}$  and  $-191^{\circ}$  is  $3\times14,28\cdot10^{-6}$  (Henning), in consequence of which  $v_{-191^{\circ}}$  becomes =7,052. And between  $-193^{\circ}$  and  $-253^{\circ}$  a  $=3\times3,9\cdot10^{-6}$  (Lindemann), which yields  $v_{-253^{\circ}}=7,047$ , so that  $v_{-273^{\circ}}=v_0$  will be =7,046.

Now  $b_{20} = \frac{5}{6} v_{20}$  follows further from  $\frac{v}{v-b} = \underline{6}$  at 20°, from which we get  $\underline{b_{20}} = 5{,}930$ . And as according to (5)  $v_{20} - b_{00} = (v_{20} - b_{20}) \left(1 + \frac{\varphi}{v_{20}}\right)$ , in which  $\frac{\varphi}{v_{20}} = \underline{0.6}$  (see IV),  $v_{20} - b_{00}$  becomes  $= 1{,}186 \times 1{,}6 = 1{,}898$ , hence  $\underline{b_{00}} = v_{00} = 5{,}218$ . Then  $v_0 - b_0 = 1{,}828:1{,}606 = 1{,}138$  is found according to (5) from  $(v_0 - b_{00}) = (v_0 - b_0) \left(1 + \frac{\varphi}{v_0}\right)$ , with  $\frac{\varphi}{v_0} = \frac{\varphi}{v_{20}} \times \frac{v_{20}}{v_0} = 0{,}6 \times 1{,}01$ , which yields  $\underline{b_0} = 5{,}908$ . As regards the (fictitious) value of  $b_g$  (at  $v = \infty$ ), the value  $7{,}116 \times 0{,}6 = 4{,}270$  follows for  $\varphi = b_g - b_{00}$  from  $\frac{\varphi}{v_{20}} = 0{,}6$ , which yields  $\underline{b_g} = 9{,}488$ . (Also from  $b_{20} = b_g: \left(1 + \frac{\varphi}{v_{20}}\right)$  the value  $b_g = 5{,}930 \times 1{,}6 = 9{,}488$  would have followed).

<sup>&</sup>lt;sup>1</sup>) From  $T_s \times 1.7 = 2578^\circ \times 1.7 = 4383^\circ$  abs.

And now the corresponding values for liquid copper. But as at 1083° C. (the melting-point of copper) the coefficient of expansion is, indeed, known to a certain extent, but not the compressibility, we must know the value of a for the calculation of  $\frac{v}{v-b}$  at 1083°. For from the equation of state follows (see I, §1)  $\frac{v}{v-b} = \frac{a/v}{RT}$ . Now we shall calculate the value  $\underline{a} = 32.63.10^{12}$  for a in III from measurements of the vapour pressure. We find for v at 1083° the value 63.57: 8.40, i.e.  $\underline{v}_{1083} = 7.568$ . Hence we have:

$$\frac{v}{v-b} = \frac{32,63 \cdot 10^{12} : 7,568}{83.17 \cdot 10^6 \times 1356} = \frac{4,312 \cdot 10^{12}}{0,1128 \cdot 10^{12}} = \underline{38,23}.$$

This value is considerably greater than for solid copper (= 6) and for ordinary liquids (± 15), but all the same perfectly plausible. For from  $\frac{v}{v-b} = \frac{f}{m} (\text{see I}, \S 1) \text{ with } m = T: T_k = 1356: 4400 = 0,3082 \text{ follows for } f \text{ the value } 38,23 \times 0,3082 = 11,8 = \text{ about } 12. \text{ From our formula } f_k = 8\gamma = 8 \times 1,76 \text{ (see above § 2) the value } 14,1 = 14 \text{ would follow for } f_k \text{ And as } f_{1083} \text{ will be somewhat smaller than } f_k \text{ as it usually is, this value agrees very well.}$ 

In IV we shall find the value 2.017 = 2 for  $\frac{\varphi}{v}$  (at  $1083^{\circ}$ ), hence about the same as for ordinary liquids  $\left(\frac{\varphi}{v} - 2.5; \text{ zie I, § 1}\right)$ . For solid substances (copper) this was only = 0.6. And knowing this value, we can easily calculate the different values of v and b.

From v:(v-b)=38,23 and v=7,568 (at 1083°) follows immediately v-b=0,198, hence  $b_{1083}=7,370$ . And then the value  $0,198\times 3,017=0,597$  follows for  $v-b_0$  at 1083° from (3), i.e.  $v-b_0=(v-b)\left(1+\frac{\varphi}{v}\right)$ , so that (fictitiously) we find  $b_0=v_0=6,971$ . And from  $b_g=b\left(1+\frac{\varphi}{v}\right)$  the value  $7,370\times 3,017$  is found for  $b_g$ , hence  $b_g=22,24$ .

Taking al that has been found together, we get the following summary, in which we have also added the results for "ordinary" substances for a comparison.

The values for "ordinary" liquids ( $\gamma = 0.9$  to 1) are:

$$\begin{cases} v_0 & v_{1/2T_k} = 1,3 \ v_0 & v = \infty \\ b_0 = v_0 & b_{1/2T_k} - \frac{14}{15} v_{1/2T_k} & (b_g)_{1/2T_k} - 4.3 \ b_0 & \frac{\varphi}{v} \Big|_{1/2T_k} 2,5. \end{cases}$$

The values for molten copper (y = 1.7) are:

M

$$\begin{cases} (v_0 = 6.97) & v_{1083} = 7.57 & v = \infty \\ (b_0 = 6.97) & b_{1083} = 7.37 & (b_g)_{1083} = 22.2 \end{cases} \begin{vmatrix} \left(\frac{v}{v - b}\right)_{1083} = 38 \\ \left(\frac{\varphi}{v}\right)_{1083} = 2. \end{cases}$$

The values for solid copper ( $v_{20}$  is at  $20^{\circ}$  C.) are:

$$\begin{cases} v_{00} = 5.22 & v_0 = 7.05 & v_{20} = 7.12 & (v = \infty) \\ b_{00} = 5.22 & b_0 = 5.91 & b_{20} = 5.93 & ((b_g)_{20} = 9.5) \end{cases} \begin{vmatrix} \frac{v}{v - b} \rangle_{20} = 6.$$

If the limiting volume  $v_{00} = 5,22$  for solid copper is assumed to be = 1.91m (in the case of cubic distribution; m is the real volume of the molecule or atom thought spherical), then we have m = 2,73, from which it follows that at  $1083^{\circ}$   $b_g = 8,14 \, m$  for liquid copper, i.e.  $= 4 \, m \times 80 \, \text{LTZMANN's}$  factor of distribution, which is accordingly about = 2 at the temperature mentioned. Also for ordinary liquids  $(b_g)_{1/2} \, T_k$  lies on an average in the neighbourhood of  $4,3 \times 1,9 \, m = 8,17 \, m$ , so that BOLTZMANN's factor is again = 2. At the absolute zero, but p = 0, we find further  $b_0 = v_0 = 2,6 \, m$  for liquid copper, and  $b_0 = 2,2 \, m$  for solid copper, so that in both cases some space is left (in consequence of the repulsive forces), which space does not vanish before  $p = \infty$   $(b_{00} = v_{00} = 1,9 \, m)$ .

#### III.

# Calculation of $\frac{a}{v^2}$ in Copper.

We will now calculate the value of a in liquid copper, which value, as will appear in what follows, may be applied to the solid state unchanged. The value of a seems therefore to be the same for all the three states of aggregation. This is not the case with b, as appears very clearly from the survey in § 3 of II.

Many years ago I drew up a theory of the solid state — without the very essential quantity  $\lambda$  however — in which v-b was retained, a passed unchanged from one state to another, and also b was supposed variable, not only in each of the two states of aggregation separately, but also at the transition from the liquid into the solid state. I did not ascribe this variability, however, to the true cause at the time, but to the so-called "quasi-association", which was then the fashion. Then another state of association was assumed by me to exist in the solid state than in the liquid state, and also the degrees of association in the two states could differ according to T and v. This hypothesis could account for much, but by no means for everything, and at present this theory may be considered as entirely discarded.

According to RUFF and BERGDAHL  $^1$ ) we have, for molten copper, the subjoined values of p, at the values of T standing above them. According to the shortened formula

$$log_{10} p^{mm} = -\frac{A_{10}}{T} + C_{10}$$
.

the values of  $C_{10}$  can be determined from the values of  $T \log_{10} p = -A_{10} + C_{10} T$  by subtraction. If for this purpose the values at the lowest and at the highest temperature are taken for the sake of accuracy (with the exclusion of that of the very lowest temperature, which in spite of the redetermination by RUFF and MUGDAN<sup>2</sup>) is not yet quite certain),  $C_{10}$  is found from

$$C_{10} = \frac{T_2 \log_{10} p_2 - T_1 \log_{10} p_1}{T_2 - T_1}.$$

From this follows for  $C_{10}$  averagely  $C_{10} = \frac{7401 - 4978}{2573 - 2378} = \frac{2423}{195} = 12,43$ .

With this values of  $C_{10}$  the values

 $A_{10} = 23880 \mid 24560 \quad 24720 \quad 24740 \quad 24710 \quad 24560$ 

are further found from  $A_{10} = C_{10} T - T \log_{10} p$ , hence on an average  $A_{10} = 24530$ . It is seen that the first value (calculated from p at 1875°) does not fit in with the others. Van Liempt 3) gave the somewhat smaller value 23600. For  $A = A_{10} \times 2,3026$  we find therefore A = 56480, hence AR becomes  $A = 4,698 \cdot 10^{12}$  with  $A = 83,17 \cdot 10^6$ .

As in 
$$log p = -\frac{A}{T} + C = -\frac{AR}{RT} + C$$
 the numerator  $AR$  is the

extrapolated heat of evaporation at the absolute zero  $^4$ ), viz.  $=\frac{a}{v_0'}$  (strictly

<sup>1)</sup> Z. für anorg. u. allg. Chemie 106, 76-94 (1919). GREENWOOD, Z. f. physik. Ch. 76, 484-490 (1911).

<sup>2)</sup> Z. für anorg. u. allg. Ch. 117, 147 (1921).

<sup>3)</sup> Z. f. anorg. u. allg. Ch. 114, 105-116 (1920).

<sup>4)</sup> For in the general formula  $\log p = -\frac{a/v}{RT} + C' \frac{a}{v}$  has been developed into a series,

viz.  $=\frac{a_0}{v_0}+\alpha$   $T+\ldots$ , in which the term with T joins the constant C' after division by RT, through which it becomes =C.

speaking  $\frac{a_0}{v_0'}$ , but a is supposed independent of T), we get

$$\frac{a}{v_0'}$$
 = 4,698 \cdot 10<sup>12</sup>.

If for the coefficient of expansion of liquid copper at  $1083^{\circ}$  the value  $65^{\circ}$ .  $10^{-6}$  is assumed  $^{\circ}$ ), the value 9,153 follows for  $D_0'$ , i. e. the extrapolated value of D at T=0 (which we want here, as appears from the derivation of the formula for  $\log p$  (cf. note 2), from the density 8.40 at  $1083^{\circ}$ ). And from this the value 63,57:9,153=6,945 is calculated for  $v'_0$ . (This value  $v'_0$ , calculated from the expansibility at  $1083^{\circ}$ , is therefore slightly smaller than the real value of  $v_0=b_0$ , which we have found above in II, § 3, v' viz. 6.97).

In virtue of this a finally becomes for liquid, hence according to the hypothesis also for *solid* copper:

$$a = 4,698 \cdot 10^{12} \times 6,945 = 32,63 \cdot 10^{12}$$

in which  $a/v^2$  is expressed in dynes per cm<sup>2</sup>. For this quality the following value is found for solid copper with  $v_{20} = 7,116$ :

$$\frac{a}{v_{20}^2}$$
 = 0,6444 · 10<sup>12</sup> (solid copper 20° C.).

#### IV.

## The Coefficient of Expansion (Solid).

We start from (4) combined with (5), viz.

$$p + \frac{a}{v^2} = \frac{\lambda + RT}{v - b} = \frac{\lambda + RT}{v - b_{00}} \left( 1 + \frac{\varphi}{v} \right),$$

which equation we shall differentiate with respect to T(p constant). Then we get:

$$-\frac{2a}{v^3}\left(\frac{dv}{dt}\right)_p = (\lambda + RT)\left(-\frac{1+\frac{\varphi}{v}}{(v-b_{00})^2} - \frac{1}{v-b_{00}}\frac{\varphi}{v^2}\right)\left(\frac{dv}{dt}\right)_p + \frac{R}{v-b},$$

when both a and  $b_g$  (in  $\varphi = b_g - b_0$ ) are supposed independent of T. Hence we get further:

$$\frac{1}{v}\left(\frac{dv}{dt}\right)_{p}\left[-\frac{2a}{v^{2}}+\frac{(\lambda+RT)v}{(v-b_{00})^{2}}\left(1+\frac{\varphi}{v}+\frac{\varphi}{v}\frac{v-b_{00}}{v}\right)\right]=\frac{R}{v-b}.$$

If in this for  $\lambda + RT$  its value from the equation of state is substituted, in which p is put = 0, we get:

<sup>1)</sup> Between 1083° and 1200° PASCAL and JOUNIAUX gave the formula  $v=v_{1083}$   $(1+62.10^{-6}~(t-1083)-560.10^{-9}~(ibid.)^2+5600.10^{-12}~(ibid.)^3)$ , of which the coefficients of the 2nd and the 3rd powers of t-1083 are much too great. Close to  $1083^\circ$  the coefficient of expansion is  $=62.10^{-6}$ . But if  $v_{1200}$  is calculated according to this formula, v becomes =7.633~(D=8.328 and not 8.32 as is given). And this would give  $\alpha=73.10^{-6}$ . As most probable value we take 65, somewhat greater than 62.

$$a\left[-\frac{2a}{v^{2}}+\frac{a}{v^{2}}\frac{v(v-b)}{(v-b_{00})^{2}}\left(1+\frac{\varphi}{v}+\frac{\varphi}{v}\frac{v-b_{00}}{v}\right)\right]=\frac{R}{v-b}.$$

i.e. after substitution of  $v-b_0=(v-b)\left(1+\frac{\varphi}{v}\right)$ :

$$a\frac{a}{v^2}\left[-2+\frac{v}{v-b}\frac{1}{1+\frac{\varphi}{v}}\left(1+\frac{\varphi}{v}\frac{v-b}{v}\right)\right]=\frac{R}{v}\frac{v}{v-b}.$$

or finally

$$a\frac{a}{v^2}\left[-2\frac{v-b}{v}+\frac{1+\frac{\varphi}{v}\frac{v-b}{v}}{1+\frac{\varphi}{v}}\right]=\frac{R}{v}.$$

If  $\frac{v-b}{v} = z$ ,  $\frac{\varphi}{v} = \omega$ , the equation becomes:

$$a\frac{a}{v^2}\left(\frac{1+\omega z}{1+\omega}-2z\right)=\frac{R}{v}.$$

i.e.

$$a = \frac{R}{a/v} \frac{1+\omega}{1-(2+\omega)z}, ... (7)$$

and this equation for a will evidently also be valid for the liquid state (p=0). It is true that then in the equation of state  $\lambda$  is absent by the side of RT, but this quantity  $\lambda$  is eliminated during the calculation. Only,  $\varphi$  is then not  $=b_g-b_{00}$ , but simply  $=b_g-b_{00}$ .

For solid copper (20° C.)  $\alpha$  is now = 3 × 17.10<sup>-6</sup>=51.10<sup>-6</sup>. We have, therefore, for the calculation of  $\omega$  (for z we found already the value  $^{1}/_{6}$  in II) with  $v_{20} = 7.116$ ,  $\frac{a}{v_{33}} = 4.585 \cdot 10^{12}$  and  $R: 83.17 \cdot 10^{6}$ :

$$\frac{1+\omega}{1-\frac{1}{6}(2+\omega)} = \frac{51 \cdot 10^{-6} \times 4,585 \cdot 10^{12}}{83,17 \cdot 10^{6}} = 2,812,$$

from which  $\omega = 0.596 = 0.6$ , of which we have already made use in II, § 3. For ordinary substances the mean value 2,5 was found for this (see I, § 1).

In molten copper at  $1083^{\circ}$   $\alpha = 65 \cdot 10^{-6}$  (see III); there we get, therefore, with  $a: v_{1083} = 32,63 \cdot 10^{12}: 7,568 = 4,312 \cdot 10^{12}$  and z = 1:38,23 (see II, § 3):

$$\frac{1+\omega}{1-\frac{1}{38.23}(2+\omega)} = \frac{65 \cdot 10^{-6} \times 4,312 \cdot 10^{12}}{83,17 \cdot 10^{6}} = 3,370,$$

from which  $\omega = 2.017 = 2$ , which value is, therefore, in the neighbourhood of that of ordinary liquids (see I, § 1 and II, § 3).

At very low temperatures (but p = 0) the value

$$a = \frac{4 PT^3}{a/v_0} \frac{1 + \omega_0}{1 - (2 + \omega_0) z_0}$$

is evidently found instead of (7), as everything remains the same; only

 $PT^4$  is now substituted for RT, which, differentiated with respect to T, yields  $4PT^3$ . Now  $\omega_0$  is  $= \varphi : v_0$  and  $z_0$  is  $= (v_0 - b_0) : v_0$ , which values will differ only little from those at  $20^\circ$  C. e.g. for solid copper (see the summary in II, § 3). Hence the coefficient of expansion  $\alpha$  will become proportional to  $T^3$  at very low temperatures, just as  $c_v$ , with which it runs parallel.

#### $\mathbf{v}$ .

# The Coefficient of Compressibility (Solid).

Now that both z=(v-b):v and  $\omega=\varphi:v$  are known, the calculated coefficient of compressibility, after substitution of these values, must agree with the coefficient determined experimentally. For according to  $(6)\frac{\alpha}{\sigma}=\frac{R}{v}\times\frac{1}{z}$ , from which we have determined the value of  $z = \frac{1}{6}$ . When, therefore, the value of  $\alpha$  comes right (and in IV this has been effected by the assumption of  $\omega=0.6$ ),  $\sigma$  must naturally also be in harmony. Only in VI and VII with the pressure and temperature coefficients of the coefficient of compressibility there can be question of a verification of our hypotheses.

Now  $\sigma^{-1} = \frac{R}{v} \times \frac{1}{\alpha z}$ , follows immediately from the above equation, hence according to (7) for  $\alpha$ , we have:

$$\sigma^{-1} = \frac{a}{v^2} \times \frac{1}{z} \frac{1 - (2 + \omega) z}{1 + \omega}, \quad (8)$$

which might also easily have been derived directly from the equation of state by differentiation with respect to v (T constant), in entirely the same way as in IV for a. However, in VI and VII we cannot make use of this result, because in this  $\lambda+RT$  has been replaced by its value from the equation of state, in which p=0 was put.

If in (8) the value 0,6444.10<sup>12</sup>, found in III, is substituted for  $\frac{a}{v^2}$ , the value 6 for  $\frac{1}{z} = \frac{v}{v - b}$ , the value 0,6 determined just now in IV from the coefficient of expansion (everything at 20° C.), we get:  $\sigma^{-1} = 0.6444.10^{12} \times 6 \times \frac{1 - (2.6:6)}{1.6} = 3,866.10^{12} \times 0.3542 = \underline{1.369.10^{12}}$ .

The value 1,370.10<sup>12</sup> was found by BRIDGMAN at 20° C., so that the agreement of course is perfect. For BRIDGMAN 1) found for pure copper (loc.

<sup>1)</sup> Compare his exceedingly important and comprehensive paper in the Proceedings of the American Acad. of Arts and Sciences 58, No. 5, p. 165—242 (1923): The compressibility of thirty metals as a function of pressure and temperature. Also in numerous other papers BRIDGMAN has considerably enriched our knowledge in this and allied regions after RICHARDS. We are greatly indebted to this investigator for his extensive and very accurate researches.

cit. p. 192) for  $-\frac{1}{v_a}\frac{\Delta v}{p} = \sigma'$ , which is practically  $= \sigma$ , in which  $v_a$  represents the volume at  $t^0$  and p = 0:

$$\sigma'_{30^{\circ}} = 10^{-6} (0.719 - 2.6 \cdot 10^{-6} p) / p \text{ in } KG/_{cm^2}$$
  
 $\sigma'_{75^{\circ}} = 10^{-6} (0.734 - 2.7 \cdot 10^{-6} p) / p \text{ in } KG/_{cm^2}$ 

If p is expressed in Dynes/cm<sup>2</sup> (in which then e.g. 0,719 must be multiplied by  $1,02 \cdot 10^{-6}$  and 2,6 by  $(1,02 \cdot 10^{-6})^2$ ), the expression becomes:

$$\sigma'_{300} = 10^{-12} (0.7334 - 2.704 \cdot 10^{-12} p)$$
 $\sigma'_{750} = 10^{-12} (0.7487 - 2.808 \cdot 10^{-12} p)$ 
 $\rho \text{ in } \frac{dynes}{cm^2}$ 

From this follows by extrapolation:

$$\sigma'_{20} = 10^{-12} (0.7300 - 2.681 \cdot 10^{-12} p),$$

so that  $\sigma_{20}$  becomes = 0,7300 .  $10^{-12}$  at p = 0, hence  $\sigma_{20}^{-1} = 1,370.10^{12}$ , as we gave above.

#### VI.

### The Coefficient of Pressure of $\sigma^{-1}$ .

As we already remarked in V, it is not allowed to start from (8), where p=0 is put, for the differentiation with respect to p, but from the equation for  $\sigma^{-1}$  derived directly from the equation of state

$$p = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b} = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b_{00}} \left( 1 + \frac{\varphi}{v} \right).$$

We find then (see also IV):

$$\left(\frac{d\mathbf{p}}{d\mathbf{v}}\right)_{t} = \frac{2\mathbf{a}}{\mathbf{v}^{3}} - \frac{\lambda + RT}{(\mathbf{v} - \mathbf{b}_{00})^{2}} \left(1 + \frac{\varphi}{\mathbf{v}} + \frac{\varphi}{\mathbf{v}} \frac{\mathbf{v} - \mathbf{b}_{00}}{\mathbf{v}}\right).$$

so that

$$\sigma^{-1} = -v \left( \frac{dp}{dv} \right)_t = -\frac{2a}{v^2} + \frac{\lambda + RT}{(v - b_{00})^2} \left( v + \varphi + \varphi \frac{v - b_{00}}{v} \right)$$
 . (a)

From this follows (T constant):

$$\begin{split} &\frac{d\sigma^{-1}}{dp} = \left[\frac{4a}{v^3} + (\lambda + RT)\left(-\frac{2\left(v + \varphi + \varphi \frac{v - b_{00}}{v}\right)}{(v - b_{00})^3} + \frac{1 + \varphi\left(-\frac{v - b_{00}}{v^2} + \frac{1}{v}\right)}{(v - b_{00})^2}\right]\frac{dv}{dp} \\ &= \frac{1}{v}\frac{dv}{dp}\left[\frac{4a}{v^2} - \frac{(\lambda + RT)v^2}{(v - b_{00})^3}\right]2\left(1 + \frac{\varphi}{v} + \frac{\varphi}{v}\frac{v - b_{00}}{v}\right) - \frac{v - b_{00}}{v}\left(1 + \frac{\varphi}{v} - \frac{\varphi}{v}\frac{v - b_{00}}{v}\right)\right]. \end{split}$$

If the value  $\left(p+\frac{a}{v^2}\right)(v-b)$  is substituted here for  $\lambda+RT$ , and the value  $(v-b)\left(1+\frac{\varphi}{v}\right)$  for  $v-b_{00}$ , we get (p=0):

$$\frac{d\sigma^{-1}}{dp} = \frac{1}{v} \frac{dv}{dp} \frac{a}{v^2} \left[ 4 - \frac{v^2}{(v-b)^2} \frac{1}{(1+\tilde{\tau}/v)^2} \left\{ 2 \left( 1 + \frac{\varphi}{v} \frac{v-b}{v} \right) - \frac{v-b}{v} \left( 1 + \frac{\varphi}{v} \right) \left( 1 - \frac{\varphi}{v} \frac{v-b}{v} \right) \right\} \right],$$

i.e. with  $\frac{\varphi}{v} = \omega$  and  $\frac{v-b}{v} = z$ :

$$\frac{d\sigma^{-1}}{dp} = \frac{1}{v} \frac{dv}{dp} \frac{a}{v^2} \frac{1}{z^2} \frac{1}{(1+\omega)^2} \left[ 4 z^2 (1+\omega)^2 - \left\{ 2 (1+\omega z) - z (1+\omega) (1-\omega z) \right\} \right],$$

or

$$\frac{d\sigma^{-1}}{dp} \stackrel{\cdot}{=} (-\sigma) \frac{a}{v^2} \frac{1}{z^2} \frac{1}{(1+\omega)^2} (-2 + (1-\omega)z + (4+7\omega + 3\omega^2)z^2).$$

According to (8)  $\sigma$  is =  $\left(1:\frac{a}{v^2}\right) \times z \frac{1+\omega}{1-(2+\omega)z}$ , so that we finally obtain:

$$\frac{d\sigma^{-1}}{dp_{(p=0)}} = \frac{1}{z} \frac{2 - (1 - \omega) z - (4 + 7\omega + 3\omega^2) z^2}{(1 + \omega) (1 - (2 + \omega) z)} . . . . (9)$$

We will now compare this with BRIDGMAN's experimental values written above.

With  $z = \frac{1}{6}$ ,  $\omega = 0.6$  (at 20° C.) the above becomes:

$$\frac{d\sigma^{-1}}{dp} = 6 \frac{2 - (0.4:6) - (9.28:36)}{1.6(1 - (2.6:6))} = \frac{60.32}{5.44} = 11.1 (p = 0).$$

According to us  $\sigma = \frac{1}{v} \frac{dv}{dp}$ , whereas in  $\sigma_1 = \frac{1}{v_a} \frac{dv}{dp}$   $v_a$  is constant with respect to p (see V). We have, therefore:

$$\frac{d\sigma^{-1}}{dp} = \frac{d}{dp} \left( -v \frac{dp}{dv} \right) = v \frac{d}{dp} \left( -\frac{dp}{dv} \right) - \frac{dp}{dv} \frac{dv}{dp} =$$

$$= \frac{v}{v_a} \frac{d}{dp} \left( -v_a \frac{dp}{dv} \right) - 1 = \frac{d\sigma_1^{-1}}{dp} - 1$$

at p=0, where  $v_a=v$ . Hence we find theoretically:

$$\frac{d\sigma_1^{-1}}{dp} = \underline{12,1} \ (p=0).$$

According to BRIDGMAN (see V)  $\sigma' = -\frac{\triangle v}{v_a p}$  is of the form of  $\alpha - \beta p$ , i.e.

$$\frac{v_a-v}{v_a}=ap-\beta p^2.$$

From this follows therefore:

$$\sigma_1 = -\frac{1}{v_a} \frac{dv}{dp} = a - 2\beta p$$
, hence because  $\frac{d\sigma_1^{-1}}{dp} = -\frac{1}{\sigma_1^2} \frac{d\sigma_1}{dp}$ :

$$\frac{d\sigma_1^{-1}}{dp} = \frac{2\beta}{\alpha^2} \ (p = 0).$$

Accordingly at 20° C is experimentally (with  $\alpha = 0.73 \cdot 10^{-12}$ ,  $\beta = 2.681 \cdot 10^{-24}$ ) (see V):

$$\frac{d\sigma_1^{-1}}{dp} = \frac{2 \times 2,681 \cdot 10^{-24}}{0,5329 \cdot 10^{-24}} = \underline{10,1} \ (p = 0).$$

The difference between 10 and 12 as differential coefficient with respect to p of a quantity which is  $=1.37 \cdot 10^{12}$  itself, may be called very small. Not only is the order of magnitude the same, but there is even almost numerical agreement; this was impossible with the earlier theories of Grüneisen, Born and others (Bridgman, loc, cit. p. 233 et seq.). Even the order of magnitude is already wrong there in many cases, up to a ratio of  $1:\frac{1}{4}\cdot 10^{-16}$ !! In comparison with this it is seen how unexpectedly well our theoretical value 12 harmonizes with the value 10 found experimentally, taking note that it would be easy through a very small modification in the value of a, which was transferred from the liquid phase to the solid phase, hence also of the value of  $\omega$ , to obtain a perfect harmony.

#### VII.

The Coefficient of the Temperature of  $\sigma^{-1}$ .

We again start from the equation (a) in VI:

$$\sigma^{-1} = -\frac{2a}{v^2} + \frac{\lambda + RT}{(v - b_{00})^2} \left( v - \varphi + \varphi \frac{v - b_{00}}{v} \right), \quad . \quad . \quad (a)$$

and must differentiate this now with respect to T (p constant). This calculation runs almost parallel with that in VI, but is somewhat longer. We can, however, obtain the result more easily by the following consideration. According to (a) is  $\sigma^{-1} = f(T,v)$ , hence  $\left(\frac{dx}{dp}\right)_t = \frac{\partial x}{\partial v} \left(\frac{dv}{dp}\right)_t$ , when for shortness we write x for  $\sigma^{-1}$ . Likewise  $\left(\frac{dx}{dt}\right)_p = \frac{\partial x}{\partial t} + \frac{\partial x}{\partial v} \left(\frac{dv}{dt}\right)_p$ .

Hence we have:

$$\left(\frac{dx}{dt}\right)_{p} = \frac{\partial x}{\partial t} + \left(\frac{dx}{dp}\right)_{t} \left(\frac{dp}{dv}\right)_{t} \left(\frac{dv}{dt}\right)_{p} = \frac{\partial x}{\partial t} - \left(\frac{dx}{dp}\right)_{t} \left(\frac{dp}{dt}\right)_{v}$$

We have, therefore, according to (a) and (9):

<sup>1)</sup> Thus in an extensive theoretical discussion of his experimental results BRIDGMAN found the value  $8.5 \cdot 10^{-40}$  (p. 230), calculated from the experiments for a certain quantity  $\beta$  (p. 232), whereas on p. 232 the quantity  $1.04 \cdot 10^{-40}$  is found for it, which he all the same calls "the same order of magnitude" (8.5 and 1). But on p. 235 the value of  $2.03 \cdot 10^{-56}$  would ensue from the coefficient of pressure, which is not less than  $1/4 \times 10^{-16}$  of the first-mentioned value!

$$\left(\frac{dx}{dt}\right)_{p} = \frac{R\left(v + \varphi + \varphi \frac{v - b_{00}}{v}\right)}{(v - b_{00})^{2}} - \frac{1}{z} \frac{2 - (1 - \omega)z - (4 + 7\omega + 3\omega^{2})z^{2}}{(1 + \omega)(1 - (2 + \omega)z)} \times \frac{R}{v - b},$$

as  $\left(\frac{dp}{dt}\right)_{v} = \frac{R}{v-b}$  immediately follows from the equation of state. With

 $v-b_{00}=(v-b)$   $(1+\omega)$  and  $\frac{\varphi}{v}=\omega$  this becomes, when  $\sigma^{-1}$  is again written for x and the indication p= constant is omitted:

$$\frac{d\sigma^{-1}}{dt} = \frac{Rv}{(v-b)^2} \frac{1+\omega z}{1+\omega} - \frac{Rv}{(v-b)^2} \frac{2-(1-\omega)z - (4+7\omega+3\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)},$$

as 
$$\frac{1}{z} = \frac{v}{v - b}$$
.

We have therefore finally:

$$\frac{d\sigma^{-1}}{dt} = -\frac{Rv}{(v-b)^2} \frac{(2-(1-\omega)z - (4+7\omega+3\omega^2)z^2) - (1+\omega z)(1-(2+\omega)z)}{(1+\omega)(1-(2+\omega)z)},$$

or

$$\underline{\frac{d\sigma^{-1}}{dt_{(p=0)}} = -\frac{R}{v} \frac{1}{z^2} \frac{1 + (1+\omega)z - (4+5\omega+2\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)}} \quad . \quad . \quad (10)$$

With  $z = \frac{1}{6}$ ,  $\omega = 0.6$ ,  $R = 83.17 \cdot 10^6$ , v = 7.116 (all this at 20° C.) this becomes:

$$\frac{d\sigma^{-1}}{dt} = -11,69.10^6 \times 36 \frac{1+(1,6:6)-(7.72:36)}{1.6(1-(2.6:6))},$$

i. e.

$$\frac{d\sigma^{-1}}{dt} = -11.69.10^{6} \times 36 \times \frac{37.88}{6 \times 1.6 \times 3.4} = -70.14.10^{6} \times \frac{37.88}{5.44} = -488.10^{6}$$

at p = 0. We have therefore theoretically:

$$\frac{d\sigma^{-1}}{dt} = -490 \cdot 10^6 \, (p = 0).$$

The following value has been found by BRIDGMAN for pure copper (p=0) (see V):

$$\sigma_{30^{\circ}}^{-1} = \frac{10^{12}}{0.7334} = 1,3635 \cdot 10^{12}; \quad \sigma_{75^{\circ}}^{-1} = \frac{10^{12}}{0.7487} = 1,3357 \cdot 10^{12}.$$

Per degree this gives an increase of  $-0.0278 \cdot 10^{12} \cdot 45 = -618 \cdot 10^6$ . But in another specimen BRIDGMAN found a much smaller value for  $\Delta \sigma$ , i.e. (in his units) against  $(0.734-0.719) \cdot 10^{-6} = 15 \cdot 10^{-9}$ , on which we based the above calculation, also  $(0.737-0.729) \cdot 10^{-6} = 8 \cdot 10^{-9}$ . On an average therefore  $11.5 \cdot 10^{-9}$ , and not  $15 \cdot 10^{-9}$ , so that we must also take only the  $^{23}/_{30}$  of the above value  $-618 \cdot 10^6$  referring to  $\sigma^{-1}$  (the pressure coefficients are exactly the same in the two specimens; only

the temperature coefficients are different). Accordingly we get experimentally on an average:

$$\frac{d\sigma^{-1}}{dt} = -475 \cdot 10^6 \, (p = 0),$$

which is again in very good harmony with the above theoretical value  $-490 \cdot 10^6$ ,

Summarizing we may, therefore, say that — at least in copper — our equation of state (4), which has now again (with the exception of  $\lambda$ ) the VAN DER WAALS' type, accurately represents, combined with b=f(v) according to (5), all the thermic quantities, and — as far as the coefficients of pressure and temperature of the compressibility coefficient are concerned — it does so with sufficient accuracy, not only as regards the order of magnitude, but also as regards the numerical value. None of the equations of state proposed earlier, were in any way adequate to do so (even apart from the inner inconsistences contained in them; see I).

When in a following Communication we shall first have discussed further the question of the degeneration of RT in the equation of state in connection with the degeneration of the Energy, we will determine the values of  $z=\frac{v}{v-b}$ ,  $\omega=\frac{\varphi}{v}$  and a for all the metals of which  $\alpha$  and  $\sigma$  are known (and this is by far the majority), and so doing again verify the said coefficients of pressure and temperature of  $\sigma$ .

Tavel sur Clarens, Suisse, 1924-1925.

Botany. — "The results of the temperature-treatment in summer for the Darwin-Tulip." (Second part). By Miss I. LUYTEN, Miss G. JOUSTRA and A. H. BLAAUW. (Communication No. 18. Laboratory for Plantphysiological Research, Wageningen.)

(Communicated at the meeting of October 31, 1925).

§ 8. Orientation of the parts to be discussed and the condition at the beginning of the experiments.

In this second part there will be discussed the most important things, observed on the material, which after leaving the eleven temperatures, was fixed in alcohol 96 % in groups of 10 bulbs after 2, 4, 6 and 10 weeks. The observations, measurements and illustrations concerning these 440 bulbs picture to us the progress in the formation of the last foliage-leaves and of the floral parts and the new main-bud in a greatly varying tempo on account of exposure to temperatures from  $1\frac{1}{2}$ ° to 35° C.

We have to avail ourselves of and refer to the detailed description of: "The periodical development of the Darwin-Tulip" bij R. MULDER, which will be published by this Laboratory as Communication No. 16. As a research it had been finished in the main before the material mentioned here was examined. Our research was founded upon those experiences and the discussion of the normal periodical course.

Referring to that paper, we shall have to cite a few passages in order to render the discussion in these pages intelligible.

In description and illustrations (figs. 4—14) all scales of the bulb have been omitted. In the axil of the inner scale a growing-point arises, yielding the main bulb in the course of the year. The state of this new growing-point (July—October) has been mentioned in the observations. (See also figs. 4—14 VPA.) Next the main-axis follows in the centre of the bulb with the first foliage-leaf, the centre of which is often found on the other side than where the new growing-point lies. This foliage-leaf often coheres at the base (see e.g. figs. 5, 6, 7, 11 LL1). In other cases the two edges just touch the new growing-point (i.e. it is divided down to the insertion-spot) (see e.g. fig. 9 LL1). The various ways in which 1st and 2nd leaf, etc. can be placed, are described by R. MULDER. After a number of foliage-leaves (which, as contrasted with the Hyacinth, are likewise inserted on the stalk) the flower with its various parts follows in the centre terminating the axis.

Founding our description on R. MULDER's discussion we shall occasionally mention the stages discernible in the formation of the Tulip flower. When the experiments were started (20 July 1922), i.e. on our placing the bulbs in the 11 different temperatures, 20 bulbs were opened and like all other material observed with the binocular microscope after staining the peeled objects in J. J. K. The condition of the bulbs was such, that with the greater 2 to 3 foliage-leaves were in formation (of the 4 to 5 which are finally formed). If, therefore, in some temperature or other after some time a growing-point is found with e.g. but 3 foliage-leaves, the process has been nearly or quite arrested in that temperature. Besides to these young foliage-leaves we draw the attention to the new growing-point, outside those foliage-leaflets, especially to the chief new growing-point, formed in the axil of the inner scale (indicated VPA in the figures). On the other new growing-points, specially in the axils of other scales, and on their further behaviour, the research already mentioned on the periodicity should be consulted.

At the beginning of the experiments this new growing-point (VPA) was visible in all 20 bulbs, fixed on 20 July 1922, viz. as an elliptical spot broadwise elongated, more or less distinctly limited; but rarely this narrow vegetation-point already showed the very first indication of a phyllom. Accordingly it may be asserted that on our starting the experiments a new growing-point (but for few exceptions without phylloms) is generally present. (Those first phylloms will become scales and this growing-point will yield the flower for May twelvemonth.)

## § 9. The development of main-axis and main-bud in the various temperatures.

Bearing in mind, that on July 20, 1922, when the experiments were started, the main-axis has split off 2 to 3 foliage-leaflets (2, 3 on an average of 17 specimens), and the new growing-point which is to form the new main-bulb is only visible in nearly all cases as an elliptical spot broadwise elongated, we shall now mention the condition after 2, 4, 6 and 10 weeks' exposure to the 11 different temperatures.

The rate at which the floral parts themselves are formed and which is of most consequence to us, will be separately discussed in § 10.

Table 9 already gives that state after 2 weeks on Aug. 4. The total length of the main-axis (where this occurs together with the flower) has been given as the average from the 10 fixed bulbs. For the number of foliage-leaves the amount has been given, counted on the 10 bulbs together. This clearly indicates the progress in leaf-formation from 23 per 10 bulbs (i.e. 2 to 3 per bulb) at the beginning, to 40 to 50 per 10 bulbs (i.e. 4 to 5 per bulb), after which the period of leaf-formation — (Stage I) ceases and the growing-point passes on to flower-formation — first by being

raised and by spherical distention (Stage II), next by the formation of the primordia of the floral parts (see § 10 and the description by R. MULDER).

As far as it could be measured after 2 weeks, the average length (height) of the new lateral vegetation-point has been given, which is to yield the main-bud; and in the last column a figure has been given, giving an impression of the division (starting with scale-formation) of this growing-point (of 10 bulbs together). In this amount (also concerning the foliage-leaves in the middle column) the description "beginning of a first division" or "beginning of a third leaflet" has been given a value of one half. The last column therefore gives an approximate representation in figures of the progress of activity of the new growing-point (e.g.  $6 \times$  beginning 1st scale  $+4 \times 1$  scale gives an amount of 7 for 10 bulbs).

TABLE 9. Condition after 2 weeks (Aug. 4).

-	and the second s											
	Total length main axis in mms.	Length flower in mms.	Total number of foliage-leaves on 10 bulbs.	Average length main-bud (new lateral growing- point) in mms.	Total number of new scales split off on 10 bulbs.							
11/20	0.95		27.5³)	_	2 .							
50	1.30	_	35 <sup>3</sup> )		4							
90	1.87	_	41.52)	-	<b>3.</b> 5							
13°	3.22	0.76	48 ¹)	0.5	8							
170	3.32	0.98	48 <sup>1</sup> )	0.5	10							
20°	2.96	0.65	48 ¹)	0.5	7.5							
23°	2.10		46 ¹)	0.3 or less	6							
251/2°	1.54	_	44 ¹)		4							
28°	0.97		31 <sup>3</sup> )		2							
31°	0.85		23 4)	-	. 1							
35°	0.84	-	- 25 <sup>4</sup> )		3							

From table 9 we directly see, that already after 2 weeks the main axis has grown longest in  $17^{\circ}$  to  $13^{\circ}$ , and decreases in length perfectly regularly towards lower and higher temperatures. This points to a most rapid progress in a temperature far below the optimal temperatures usually mentioned in botany. The same may be said of the flower as far as its length could be measured (in  $13^{\circ}$ — $20^{\circ}$ ). The leaf-formation is finished in the temperatures  $13^{\circ}$ — $25\frac{1}{2}^{\circ}$ , accordingly also in temperatures above

<sup>1)</sup> Leaf-formation finished, 4 to 5 leaves formed per bulb; flower-formation in nearly all cases started or even far advanced (see § 10 and fig. 3).

<sup>2)</sup> A few still in stage I. (forming leaves).

<sup>3)</sup> By far the most in stage I.

<sup>4)</sup> All of them in stage I.

20° and has progressed from 2—3 to 4—5 leaves per bulb. In higher and lower temperatures that leaf-formation is not yet finished. As will be noticed here and later on, the tulip does not progress at all in growth and formation of organs in 31° and 35° or is much behind 5° and even  $1\frac{1}{2}$ °. Here the difference with the hyacinth, where 5° completely inhibits, is great (see 1924, literature cited, conclusion 3rd part). In the main-bud and its incipient divisions the result is the same: in 17°, next in 13° and 20° the most rapid development 1).

In the tables 10, 11 and 12 the condition has been given after 4, 6 and a good 10 weeks. In order to get a survey of the progress of various processes in the course of the weeks for a special temperature, these 4 tables should be mutually compared. In tables 10—12 the length of the leafless part of the stalk has been inserted (from the highest leaf to the base of the flower), which appears to be perfectly parallel with the total length of the main-axis.

A mutual comparison of the tables with all these averages shows, that in the course of the weeks the *celerrimum* is moved a little lower; initially found at  $17^{\circ}$ , it definitely approaches  $13^{\circ}$  later on. This as to the rate of growth, the lengthening of the organs. With respect to the *number* of new organs at the young growing-point  $17^{\circ}$  remains the most rapid,  $13^{\circ}$  and  $20^{\circ}$  are about equally favourable. But the differences are slight.

TABLE 10. Condition after 4 weeks. (Aug. 18).

	Total lenght main-axis in mms.	Length flower in mms.	Number of leaves per 10 bulbs.	Length leafless part of stalk.	Length main-bud.	Average number of new scales split off per 10 bulbs.
11/20	1.5	-	35		0.2	5
50	2.2	_	38		0.2	5
90	4.4	-	45	1.4	0.4	15
130	8.2	· 1.2	48	2.8	1.5	25
170	7.2	1.6	51	2.4	1.4	25
200	5.1	0.9	48	1.6	0.8	20
23°	3.7	0.6	45	1.2	0.4	15
251/2°	2.7	0.3	49	1.0	0.1	7.5
280	1.2	_	39		_	5
310	1.1	_	34	_	_	5.
35°	0.9	_	30			2.5

<sup>1)</sup> The fact that at 35° this number of divisions (3) is somewhat higher than at 28° and 31° is sure to be accidental; it should not be attached any value to; see tables 10, 11 and 12.

TABLE 11. Condition after 6 weeks. (Sept. 1).

	Total lenght main-axis in mms.	Length flower in mms.	Number of leaves per 10 bulbs.	Length leafless part of stalk.	Length main-bud.	Total number of new scales per 10 bulbs.
11/20	1.7	_	34	_	0.1	5
50	3.5		49	_	0.4	7.5
90	8.3	0.65	51	2.9	1.3	15
130	14.0	4.1	53	5.3	2.8	30
170	11.3	3.4	48	4.0	2.1	32.5
200	7.9	2.0	43	2.8	1.6	30
230	5.9	1.2	43	1.8	1.1	25
25 <sup>1</sup> / <sub>2</sub> °	4.3	0.85	41 .	1.3	0.5	15
<b>2</b> 8°	2.1	_	37	_		5
31.0	1.4	<u> </u>	,37	_		2.5
35°	0.9	-	30			2.5

TABLE 12. Condition after  $10^{1}/_{2}$  weeks. (Oct. 1).

	Total length main-axis in mms.	Length flower in mms.	Number of leaves per 10 bulbs.	Length leafless part of stalk.'	Length main-bud.	Total number of new phylloms per 10 bulbs.
11/20	3.1	_	44		0.2	5
50	10.2	0.8	45	2.9	1.2	17.5
90	21.9	4.3	46	46 7.3 3.5		30
13°	26.3	8.3	54	54 9.8 4.8		<del>4</del> 5
170	21.9	8.0	48	7.5	4.3	50
<b>2</b> 0°	16.8	6.0	44	5.5	3.8	45
23°	10.6	2.7	41	3.6	2.8	37.5
25 <sup>1</sup> /2°	9.1	2.7	38	2.7	1.6	<b>27</b> .5
280	6.3	1.6	43	1.8	0.7	17.5
310	3.1	0.3	50	0.9 —		5
35°	± 1.0	_	28	-	_	2.5

In 35° the processes measured have fairly come to a standstill, so that even the main-axis has grown scarcely longer after 10 weeks. In 5° everything progresses, though slowly; even in  $1\frac{1}{2}$ °, where finally after 10 weeks the average number of foliage-leaves (4 to 5 per bulb) has been formed, though they have not been completely split off.

In the next § 10 we shall discuss the development of the flower in those temperatures; which is of most importance here.

# § 10. Development of the whorls of floral parts in the various temperatures.

The main-axis of the Tulip is terminated by one flower with its various whorls of floral parts. How those whorls succeed each other, at what time this usually occurs in our climate in field-culture, what stages we have to distinguish in the flower-formation, all this is discussed in the research on: "The periodical development of the Darwin-Tulip" by R. MULDER.

The number of the various floral parts originating under the influence of various temperatures, we already described in the first part (see § 5), in which we observed, that the number of foliage-leaves depended but little or not at all upon the temperature, the number of floral parts to a

strong degree.

After having discussed some organs in § 9, we shall briefly describe the tempo of progress of the flower-formation in the period, that the bulbs have been exposed to the 11 different temperatures. This may be done in a concise form with the aid of fig. 3, where in the form of a "dot-curve" the rate of flower-formation after 2, 4, 6 and a good 10 weeks may be read. The 10 bulbs examined from 11 temperatures at 4 points of time have been given as dots at the height each of them has reached according to its flower-development.

If still belonging to stage I, they have been placed (sometimes e.g. in 2 rows of 5) in the lower half of the square concerned. Are they in Stage I+ or Stage I to II, they are found in the upper half. The height of the squares denoting Stage I is but  $^2/_3$  of the height of those denoting the further stages. For those later stages the dots in the squares have been placed on three different heights. If they are in the lowest part, it means that this stage is not quite finished, e.g. III—, V—. They are placed in the middle when exactly that stage is found. If in this case the number is fairly large, the dots have been put in 2 rows close below and above the centre of the square. In the upper (3rd part) dots were inserted when the stage was somewhat more advanced (e.g. indicated as V+ or V to VI, etc.).

Briefly rendered the stages I-VII indicate:

I. Still forming foliage-leaves, growing-point flat and low.

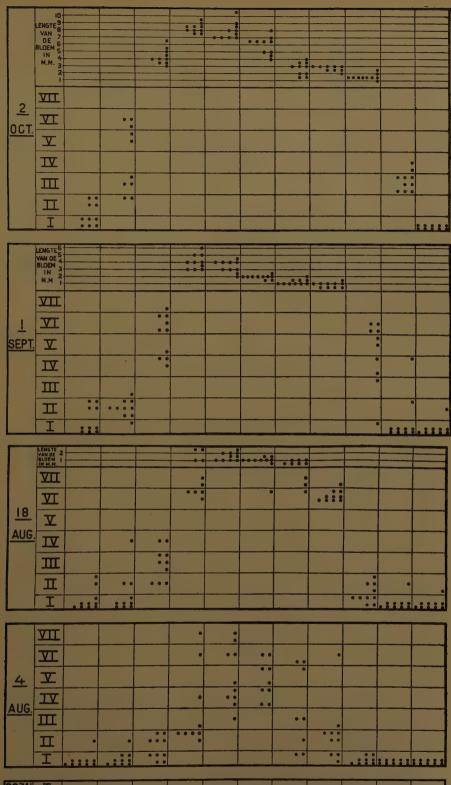


FIG.3 1,5° 5° 9° 13° 17° 20° 23° 25,5° 28° 31° 35°

- II. Growing-point broad, rounded, raised.
- III. Outer tepals all split off as individual primordia.
- IV. Inner tepals all split off as individual primordia.
- V. Primordia of the outer whorl of stamens quite finished.
- VI. Primordia of the inner whorl of stamens quite finished.
- VII. Carpels visible as individual formations.

(See the further description and more detailed explanation by R. MULDER.)

If this stage is reached and this is very soon in favourable temperatures, the length of the flower is plotted on the ordinates. But we must draw the attention to the fact, that flower-stage and flower-length do not join perfectly together and accordingly could not properly be joined in a curve. These two parts have therefore been separated by a slightly heavier horizontal line. In higher temperatures as 23° and 25½° the flower is much smaller, when all parts already have been formed. For instance in 25½° on Sept. 1 Stage VII is exceeded by all, the average height of the flower being only 0.85 mm., in 13° on Aug. 18 only half the number of flowers has reached or exceeded Stage VII, while the average length of all the ten flowers is 1.2 mm.; of the 6 in Stages VI to VII it is 0.9 mm. If for instance in 25½° on Aug. 18 ± Stage VI+ has been reached, the flower-length is only 0.3 mm., the 6 specimens however, which only reached Stage III to IV in 9°, have a length of 0.55 mm.

Bearing in mind that the two parts of the curves below and above the heavier line cannot be perfectly joined, we may draw the following conclusions from this figure from which the whole result may be read.

The temperatures 17° and 20° cause the most rapid flower-formation, next 13° and 23°. This is already visible after 2 weeks, when the flower-formation (in those temperatures) is in progress and this proportion is fairly equal after 4 weeks. In 17° all flowers are finished, in 20° 9 of the 10 flowers, accordingly within 4 weeks about two foliage-leaves and next all whorls of floral parts have been formed. In 23° 7 of the 10, in 13° about 5 of the 10 bulbs have finished forming their floral parts.

As mentioned before the parts formed are larger in the low temperatures (e.g. 13°) than in 20° and 23° and besides the floral parts are more numerous in 9° and 13° than in the higher temperatures. (See 1st part § 5).

After 6 weeks in 13° all flowers are ready and longest, in 23° all of them are ready but considerably smaller and but little increased in length. But after 6 weeks in  $25\frac{1}{2}$ °, all bulbs have likewise finished their flowers and both on Sept. 1 and Aug. 18 there is a mutual uniformity in their formation (the dots are close together).

In 9° and 28° the bulbs are equally far advanced after 6 weeks (Stages IV, V, VI in the main), and on Oct. 2 accordingly after a good 10 weeks, the bulbs in 9° and 28° have likewise finished all their flowers. Of the size

and the variation in size of the flowers completed in 9° to 28°, the curve of dots of Oct. 2 above the heavier line gives a clear representation.

It is a striking fact, that whereas on Sept. 1 all flowers are ready in 13° to 25½°, there is not one completed in 9° and 28° (the one dot in the lower part of the square 9° is in Stage VII—, i.e. the carpels have not all been split off or the division into individual parts is not entirely completed). Likewise: when on Oct. 2 all flowers are ready from 9° to 28°, there is not a single one finished in 5° and 31°. Flower-formation therefore proceeds at a much slower rate in 5° and 31° than in 9° and 28°.

Finally on considering the extreme temperatures  $1\frac{1}{2}^{\circ}$  and  $35^{\circ}$  we find, that  $35^{\circ}$  inhibits the flower-formation more than  $1\frac{1}{2}^{\circ}$ , where a few still get further than Stage II (II+).

### § 11. A comparison between Tulip and Hyacinth.

Now that we have made this research on two plants (Hyacinth and Tulip), a comparison is interesting. We shall be brief here but we shall revert to the subject later on.

Hyacinth and Tulip show this typical difference in the rate of flower-formation in various temperatures, that the celerrimum of flower-formation in the Tulip is found in lower temperatures than in the Hyacinth.

For this we refer to the dot-curve for the Hyacinth given in a previous paper (see 1924). For the sake of comparison we shall add some data. The rate of the flower-forming process for the Tulip has been judged from an exposure for 4 and 6 weeks (July 20 to Aug. 18 and Sept. 1), for the Hyacinth from an exposure of 8 weeks to those temperatures (July 7 to Sept. 1). It should be borne in mind that in the case of the Tulip we have to deal with one central flower, in that of the Hyacinth with the formation of a cluster of smaller flowers, where, however, the rate of flower-formation was judged only from the state of one of the lower flowers.

The order of succession of the temperatures for the rate of completing the flower in the Tulip, and of the lower flowers of the Hyacinth-cluster is about as follows:

Darwin-Tulp.	Hyacinth (Queen of the Blues)
17° and 20°	· 25¹/2°
13° and 23°	20° and 23°
25 <sup>1</sup> / <sub>2</sub> °	28°
9° and 28°	

In the Tulip the flower is ready in 10 weeks in a temperature-range from 9° to 28° C.

In the Hyacinth the lower flowers of the cluster are completed in 12 weeks in a much narrower range (20° to 28° C.).

Strongly contrasted are 13° and especially 9°, when in the Tulip all flowers are completed with an extra large number of floral parts, whereas in 9° not a single flower is finished in the Hyacinth. Likewise in 13° and 17° we often find failures or a slight number of flowers on the cluster of the Hyacinth.

In the Hyacinth 5° causes a total standstill (though there is some action at  $1\frac{1}{2}$ °), in the Tulip albeit the flower develops slowly in 5°, yet it advances a good deal in 10 weeks; neither does  $1\frac{1}{2}$ ° cause an absolute cessation.

Whilst the Hyacinth slightly progresses in flower-formation in  $35^{\circ}$  (about equally far as  $9^{\circ}$ ), in the Tulip this high temperature means absolute cessation.

Accordingly it is clear in all respects that the processes of flower-formation in the Tulip occur in lower temperatures than are necessary for the Hyacinth. It should be borne in mind that in our case a "late" variety of Tulip is compared to the "late" variety Queen of the Blues. (The odds are, that with "early" varieties the flower-formation is adapted to lower temperatures than with "late" varieties. Indications of this were found in one of our researches on the Hyacinth.)

We know that in culture the Darwin-tulip is reckoned among the late tulips. But this research has also taught us, that later or earlier flowering greatly depends upon the store-temperature in the previous summer. So the Darwin-tulip stored in  $25\frac{1}{2}^{\circ}$  to  $28^{\circ}$  flowers at the usual time; if, however, the bulbs have been stored in low temperatures, the period of flowering outside in the field is about 3 weeks earlier in the same year.

Seeing we compared a late variety of Tulips with a late variety of Hyacinths, we may accept that the difference in temperature-effect stated here will hold good for earlier Tulips and earlier Hyacinths. Moreover it is in perfect correspondence with the experience we have in our climate concerning the care of the field-cultures in winter (i.e. in a much later stage): The Tulip is much more proof against the cold of winter than the Hyacinth. We hope to revert to these subjects later on in a comparative survey of the periodicity in flower-formation and growth.

### § 12. Further conclusions and discussion of figures 4—14.

After the exposure to 11 greatly diverging temperatures for various periods of time, we want to draw some conclusions from this, leading to further experiments to be described later on. For instance in the 3rd part the result will be mentioned of 27 combinations of temperatures based upon the experience obtained in the 1st and 2nd parts (§ 1—12). As a most favourable treatment for common field-cultures we could choose the same

treatment as for the Hyacinth: in 26° C. till Sept. 1, next a month cooler at 17°.

This 10. because the flowers, though slower in formation in 26° than in 17° and 20°, are formed very regularly; 26° is by no means a celerrimal temperature, but does belong among the optimal temperatures for the flower-formation.

- 20. because for the rest the flowering-period in the field is "normal" for this late variety of tulips.
- 30. because in 26° the whorls of floral parts approximate the definite numerical groundplan 6—6—3 rather closely.
- 40. because the foliage developing later, is among the best. (See also 3rd part.)

Since on Sept. 1, i.e. 6 weeks after 2 or 3 foliage-leaves had been formed, the rest of the leaves and all floral parts are in formation in  $26^{\circ}$ , transmission to a cooler temperature, e.g.  $17^{\circ}$ , seemed desirable to us with a view to stretching. Yet we shall repeatedly compare this combination  $26^{\circ}$  followed by  $17^{\circ}$  with other combinations and we shall revert to it in the 3rd part and later in the 4th.

This orientation gives us already a clear indication for the *celerrimal* flower-formation and flowering (with respect to *early flowering*), to which we shall revert in later publications.

To this we may attach experiments on retardation (change of time) of the plant, either through high or through low temperatures. Researches on this subject have been in progress for a long time; they require much time, but will be discussed later.

We shall now give a brief description of the folding plate enclosed with figs 4—14. This gives the effect after 4 weeks' exposure to 11 temperatures: for each temperature one object has been chosen, representing a fair average of the 10 specimens, drawn from nature by Mr. VAN TONGEREN, magn. 25 ×. The illustrations represent: the new growing-point that is to yield the main-bud (= later main-bulb) (lying in front; always at the bottom on the plate); next the young foliage-leaves formed, all or part of them removed in order to show the flower or the growing-point of the flower.

This series is given here:  $1^{\circ}$ . as a true survey of the effect of  $1\frac{1}{2}^{\circ}$  to 35° in 4 weeks;  $2^{\circ}$ . to provide material for study for instruction or for the grower who wants to judge of his plants himself.

Abbreviations: VPA = the new lateral growing-point which is to yield the main-axis, sometimes already showing R1, R2 etc. = 1st, 2nd etc. scale split off for a new bulb; when a scale has been removed to show the further new growing-point, we find LR1 = scar 1st scale.

L1, L2 etc. = 1st, 2nd etc. foliage-leaf on the main-axis.

LL1, LL2 etc. = scars of the 1st, 2nd etc. foliage-leaves removed.

T = Tepal; only distinguished as T I and T II, when inner and outer whorl are distinctly separated.

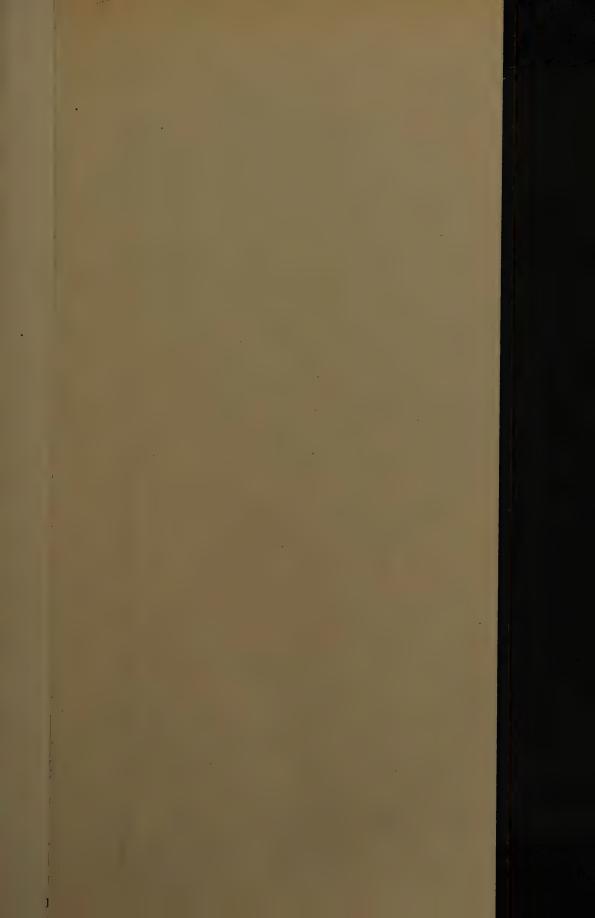
M = Stamen; whorls distinguished into M I and M II when there is no doubt.

VD = Carpel.

After the descriptions in the previous § § of the 1st and 2nd parts further explanation will be superfluous. A detailed mention has been made of the number of floral parts. In 13° we find a type with a tepal, a stamen and a carpel more than the definite numerical groundplan (i.e. 774). In 17° a very regular tetramerous one (884). In 20° 3 outer tepals (T I) and 3 inner (T II), but the inner tepal to the right has an appendix. Opposite to the larger part of this tepal we find one stamen (anther) (M), moreover opposite to the smaller lengthening-piece (in the figure above it) an additional small stamen; next there is an extra stamen of normal size, so that the flower is composed as follows: Tepals 3 + 3 (or  $3\frac{1}{2}$ ), Stamens 8 (7 normal, 1 very small), Carpels 4, 2 larger and 2 smaller ones. So numerous cases may occur. The number of parts and the number of irregularities is largest in 13°, next in 9° (after sufficiently long exposure) and in 17°. The large number of floral parts may be due to the larger surface of the vegetation-point in low temperatures, which provides more room for formation. It is true, that by the time the flower in 17° and 20° is ready, the axis is longer than in 9°, while in 9° there averagely arises a larger number of parts, but the flower-formation progresses rapidly in 17° and 20° and when the flower in 9° is finished, the axis is surely as long as at the time when the flowers in 17° and 20° were completed.

Bij the side of a pure and regular tetramerous type of  $17^{\circ}$  we find a pure trimerous type in  $23^{\circ}$  (at the bottom to the right there is an M I with a small lengthening-piece to the left, while the carpel VD on the opposite side also is a little larger than the other carpels). The illustration of the specimen of  $25\frac{1}{2}^{\circ}$ , of a purely trimerous form, has not yet differentiated its carpels. (Stage VI). The very backward state in  $1\frac{1}{2}^{\circ}$ ,  $5^{\circ}$ ,  $31^{\circ}$  and  $35^{\circ}$  after 4 weeks should be noted, for the rest this plate needs no comment, and illustrates many things treated of in detail in previous §§. It is a faithful rendering of what has been schematically represented in figure 3, Aug. 18.

In parts 1 and 2 (§§ 1—12) abnormal formations in the Tulip-flower were repeatedly mentioned and everyone who is somewhat familiar with the Tulip, knows how frequent, e.g. transitions from leaves to floral parts and of floral parts mutually, are. In some literature to be cited by us at the conclusion of part 3, we shall refer to papers in which many of those abnormalities are discussed. In the main however these descriptions





deal with the "doubling" of the flowers. So we particularly refer to the detailed descriptions given by K. ORTLEPP (1915) in his Monography of such abnormalities in full Tulips. In the first part we already pointed out, that the great number of floral parts due to lower temperatures, holds good for all whorls of floral parts and is in no way comparable with the "doubling" of flowers, which has been repeatedly described and where an abnormally great number of petaloid parts originate not only through splitting but especially at the expense of more inward whorls of floral parts.

In the first part it was also mentioned, that several kinds of deviations were fixed and partly recorded, that not until later we could treat the various teratological phenomena found in the Hyacinth and Tulip after various treatments and a discussion of them had to be omitted here. After describing in the first part the result of 44 temperature-treatments of 440 plants in the fields and tracing in the second part the effect of 11 temperatures on 440 objects in embryonic state, we must not conclude without at least giving an enumeration of the kinds of deviations we met (apart from the number of deviations already discussed in part I):

Highest foliage-leaf: split at the apex (occurring also with other foliage-leaves).

Highest foliage-leaf: inserted close below the tepals.

Highest foliage-leaf: insertion-spot grown with the top part of the stalk in longitudinal direction.

Highest foliage-leaf: coloured more or less like a tepal.

Highest foliage-leaf: fringed at the apex.

Flower: Never appeared or withered very early (after very long exposure to very low temperatures).

Flower: remaining green or greenish.

Tepal: more or less like a foliage-leaf, in colour, structure and position (forming transitional cases to the 4th case mentioned sub "highest foliage-leaf").

Tepal: more or less resembling a stamen.

Stamen: more or less resembling a tepal.

Stamen: 2 coherent stamina.

Stamen: 2 anthers on one filament.

Stamen: filament without anthers.

Stamen: withered anthers (especially after exposure to the very low and very high temperatures).

Stamen: more or less coherent with a carpel. Carpels: more or less coherent with a stamen.

Carpels: unequal in size.

Carpels: carpels remaining more or less open, so that the ovules lie bare.

Considering the whole number of floral parts mentioned in all flowers observed, the number of deviations was not very large. However it was largest in consequence of half or complete failures of flowers after a too long exposure to e.g. 11/2° and 35°, after which the less extreme temperature in the ground was no more capable of causing a good flower-formation in due time. They were rather numerous in such temperatures, as  $9^{\circ}$  and  $13^{\circ}$ , where the largest number of floral parts originate.

The least deviations occurred after exposure to rather high temperatures (especially  $25\frac{1}{2}^{\circ}$ ), when the floral parts were formed in a slow tempo (see § 10) and the numerical groundplan frequently occurred (see § 5).

Wageningen, Oct. 1925.

Mathematics. — "On a Function which Assumes any Value on a Non-Enumerable Set of Points in any Interval". By Prof. J. WOLFF. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of November 28, 1925).

LEBESGUE has given an example of a function which assumes any value in any interval. This example is constructed by means of decimal developments. The points x where the function assumes a given value y, form an enumerable set for any value of y different from zero.

By the aid of a perfect set of points P of which each pair of points has an irrational distance, (cf. These Proceedings 27 p. 95 and a communication of Prof. L. E. J. BROUWER in these Proceedings 27 p. 487) we shall construct a function which in any interval assumes any value on a non-enumerable set of points.

- 1. Any perfect set of points P may be split into sets of points having the cardinal number c which are the elements of a set of the cardinal number c. For the points of P may be brought into (1,1) correspondence with the points of a plane  $\pi$ . To any straight line of a parallel pencil in  $\pi$  there corresponds a sub-set of P which has the cardinal number c. No pair of these sub-sets has any point in common.
- 2. Let P be a linear perfect set of points of which any pair of points has an irrational distance. We call the rational numbers from minus infinite to plus infinite  $r_1, r_2, \ldots$  Further we call  $P_k$  the set which may be derived from P by adding  $r_k$  to every number of P. For  $i \neq k$   $P_i$  and  $P_k$  have no point in common. According to § 1 we split P into sets of points D(y) of which each has the cardinal number c and which correspond one by one to the real numbers p. The set which is derived from p (p) by adding p to every number of p (p), we call p (p).
  - 3. Now we define a function f(x) in the following way:

$$f(x) = 0$$
, if x does not lie in any  $P_k$ ,  $k = 1, 2, 3, ...$   
 $f(x) = y$ , if x lies in  $D_k(y)$ ,  $k = 1, 2, 3, ...$ 

Let y be an arbitrary real number and let I be an arbitrary interval. D(y) contains a point of condensation  $\xi(y)$ , i.e.: in any interval containing  $\xi(y)$ , D(y) is non-enumerable. I contains a point  $\xi_k(y)$  which is derived from  $\xi(y)$  through addition of a rational number  $r_k$ , hence  $D_k(y)$  is non-enumerable in I. And as f(x) = y in  $D_k(y)$ , f(x) assumes the value y in a non-enumerable sub-set of I.

Hence in any interval our function assumes any value on a non-enumerable set of points.

4. We must remark that f(x) has any rational number as period; and also that f(x) only differs from zero on a set of the measure zero, to wit on the set which we find by combining  $P_1, P_2, \ldots$ , after excluding from each of these perfect sets of the measure zero the points where

$$f(x) = 0$$
, hence  $D_k$  (0). Accordingly  $\int_{-\infty}^{\infty} f(x) dx = 0$  in the sense of LEBESGUE:

f(x) is equivalent to the function which is identically zero. All  $P_k$  are nowhere dense, hence the set of the points x where  $f(x) \neq 0$  belongs to the first category of BAIRE.

Let us finally remark that all this almost literally holds good if for the x-set and for the y-set we substitute spaces of any number of dimensions. Accordingly it is for instance possible to define three functions u, v and w of x so that in the corresponding representation of the straight line  $-\infty < x < \infty$  on the space (u, v, w) the image of each x-interval covers the whole space a non-enumerable number of times.

Utrecht, September 1925.

Anatomy. — "The relation of the cerebellum weight to the total brain-weight in human races and in some animals". By C. U. ARIËNS KAPPERS.

(Communicated at the meeting of November 28, 1925).

In the following pages I shall give some figures concerning the total brainweight and the cerebellum weight in the Dutch, Chinese and Japanese adding some figures concerning the same relation in animals.

I have been induced to this work amongst other things by the fact, that TOPINARD 1) seems to consider the relation of the cerebellum weight to the total brain weight (T. B. W.) of some value for anthropological studies and, on account of the weighings of CLAPHAM 2), thinks himself justified to the conclusion that the relative cerebellum weight in the Chinese is less than in Europeans.

Another motive to examine this relation is that — in connection with the somewhat different character of the Mongolian brain compared with that of the average Dutch brain — it seemed not impossible that the cerebellum in the Chinese might be different in its weight relation to the total brain from the average Dutch.

Before entering upon the results of my researches, I will briefly review the literature on the relative cerebellum weight in adult man 3).

KRAUSE <sup>4</sup>), examining this subject in Germans, stated the average cerebellum weight percentage in men to be 1/9 or 11.1~0/0, in women 1/8 or  $12^{1}/2~0/0$ , giving an average absolute figure of 128 gr.

Parchappe 5) on the contrary (in the French) found a larger cerebellumpercentage in men  $(11.8\,^{0}/_{0})$  than in women  $(10.8\,^{0}/_{0})$  and gives the former an average absolute cerebellum weight of 160 gr., with an average T. B. W. = 1352 gr., in women an average absolute cerebellum weight of 133 gr., with an average T. B. W. = 1229 gr.

Somewhat lower figures are mentioned by HUSCHKE 6): in men between 10 and 80 years he found  $10.95 \, ^{0}/_{0}$ , in women of the same age  $10.69 \, ^{0}/_{0}$ , so in the average  $10.82 \, ^{0}/_{0}$ .

<sup>1)</sup> TOPINARD, Eléments d'Anthropologie générale. Paris 1885, pag. 578. "Chez les hommes la plus forte proportion de cerveau se rencontre chez les Chinois et les Caroliniens de M. CLAPHAM et inversement la moindre proportion de cervelet et de moëlle allongée réunis".

<sup>&</sup>lt;sup>2</sup>) CROCHLEY CLAPHAM, The brain weight of some Chinese and Pelew Islanders. Journal of the Anthropological Institute of Great Britain and Ireland. Vol. VII, 1878, pag. 89.

<sup>3)</sup> I shall not discuss here the interesting results of PFISTER on the relative cerebellum weight in children (Das Hirngewicht im Kindesalter, Arch. f. Kinderheilkunde Bnd. 23, 1897, p. 164).

<sup>4)</sup> KRAUSE, Handbuch der menschlichen Anatomie. Cited here after the third ed. 1879. Vol. 11, pag. 763.

<sup>5)</sup> PARCHAPPE, Recherches sur l'Encéphale, sa structure, ses fonctions. Ière Mémoire. p. 99. Paris 1836.

<sup>6)</sup> HUSCHKE, Schädel, Hirn und Seele der Menschen und der Tiere nach Alter, Geschlecht und Raçe. Mauke, Jena 1854, pag. 75.

Figures similar to those of PARCHAPPE were found by BOYD <sup>1</sup>) ( $3^{\circ}$  11,90/0 and  $2^{\circ}$  11,440/0) on account of 2500 cases in St. Marylebone's Infirmary and the Somerset County Asylum. MEYNERT <sup>2</sup>) on the contrary found in men 10,50/0 only, in women 10,60/0.

CRICHTON BROWNE <sup>3</sup>), examining 400 postmortems at the West Riding Asylum, again gave a higher average:  $11,33\,^{\circ}/_{\circ}$ .

The latest statistics concerning this matter are composed by REY, on account of the figures, registered by BROCA in 273 men and 137 women.

REY 4) found the average to be in men  $10,66\,^{\circ}$ /<sub>0</sub>, in women  $11,03\,^{\circ}$ /<sub>0</sub>, consequently a total average of  $10,84\,^{\circ}$ /<sub>0</sub> 4).

The most important weighings for my subject are those published by WEISBACH<sup>5</sup>) for the different nations of the former Austro-Hungarian monarchy, belonging with those of BOYD and REY to the most useful ones covering the largest material, and — in contrary to those of BOYD and REY (BROCA) — concerning mostly neurologically normal people. WEISBACH's figures are also important for my purpose, since they include the Magyars, a race being largely Mongolian.

WEISBACH then found in the different populations of the former Austro-Hungarian monarchy the following relations:

Nations	Number examined brains.	Aver. T.B.W.	Aver. weight Cerebell.	Aver. <sup>0</sup> / <sub>0</sub> cerebell.
Magyars	46	1322.86	139.74	10.56 %
Roumanians	13	1326.58	142.83	10.76 "
Italians	40	1301.37	139.82	10.74
Poles	11	1320.59	140.08	10.60 "
Ruthenians	18	1320.63	141.55	10.71 "
Slovakians	11	1310.74	142.56	10.87 "
Czechs	25	1368.31	146.28	10.69 "
South-Sclavonians	8	1305.14	139.56	10.69 "
Sclavonian women	14	1174.95	129.60	11.03 "
Germans .	46	1314.50	142.20	10.81 "
German women	16	1180.15	125.56	10.63 "

<sup>1)</sup> BOYD, Tables of weight of the human body and internal organs etc. arranged from post-mortem examinations. Philos. Transactions of the Royal Society of London. B. Vol. 151, 1861. I calculated these percentage figures after the figures, given by BOYD on pag. 262.

<sup>&</sup>lt;sup>2</sup>) MEYNERT, Das Gesamtgewicht und die Teilgewichte des Gehirns. Vierteljahrsschrift für Psychiatrie 1867. Bnd 1. Quoted after Ziehen; I could not obtain the original.

<sup>&</sup>lt;sup>3)</sup> CRICHTON BROWNE, On the weight of the brain and its component parts, in the Insane. Brain. Vol. I, 1879.

<sup>4)</sup> REY. Les poids du cervelet, du bulbe, de la protuberance et des hémisphères d'après les régistres de Broca. Revue d'Anthropologie. 2ième serie, Tome VII, p. 193. 1884.

<sup>&</sup>lt;sup>5</sup>) WEISBACH, Gewichtsverhältnisse der Gehirne Oesterreichischer Völker. Archiv für Anthropologie. I, 1867.

In this table the Magyars have the smallest relative cerebellum weight, a fact I shall return on later (see pag. 135).

Moreover WEISBACH observes that he found great individual differences in the relative cerebellum weight, even with approximatively equal total brain weights.

According to him these differences may be explained only partly by regressive alterations of the different brain parts with age (in Germans in men the cerebellum diminishing relatively more than the cerebrum, while in women the cerebrum should exhibit more regressive changes in old age).

I need not say that the number of women, examined by WEISBACH is too small to justify this conclusion as a constant fact.

On account of one male cerebrum of 91 years and two female ones of 92 and 93 years TOPINARD concluded inversively (l. c. p. 579). My own figures show the value of such conclusions, as I registered a man 76 years old showing a cerebellumpercentage of 10.62 followed by another, 76 years old, with a percentage of 8.98, followed again by a man, 87 years old, with a cerebellumpercentage of 12.12  $^{0}$ /<sub>0</sub>. Amongst the women I have one 76 years old, with a cerebellumpercentage of 11.24 and another, 80 years old with 9.72  $^{0}$ /<sub>0</sub> cerebellum. We ought to view these cases individually without generalising. In this matter I absolutely agree with REY, saying "les poids absolus et les poids relatifs du cervelet, du bulbe, de la protubérance et des hemisphères présentent de continuelles oscillations où il est difficile, sinon impossible de saisir l'influence de l'âge."

Moreover WEISBACH (l.c. p. 316) supposes the height of the body to influence more the cerebellum than the cerebrum. Generally in larger men he found the cerebellum weight to be relatively larger.

My own material of human brains being too small, and containing too few cases, in which the body length 1) was noted, I was unable to verify this on human material.

On account, however, of my weighings of animal cerebella I shall return to the influence of the stature.

CLAPHAM's figures on the Chinese are useful for our comparison with a correction only (see below) since this author did not weigh the severed cerebellum, but the cerebellum connected with the pons and medulla oblongata (in 16 cases).

Owing to the above it is interesting to know the figures, found by myself in 7 Northern-Chinese, 15 Chinese from the Dutch East-Indies, totally 22 Chinese cerebra and in 8 Japanese brains.

Thanks to Prof. DEELMAN, Dr. DIJKSTRA and Dr. HAMMER I have been able to compare these figures with those found in 25 Dutch brains (13 from Groningen and 12 from Amsterdam W.G.).

<sup>1)</sup> In the average the stature of the Chinese (especially of the Northern-Chinese) is not smaller than that of the Dutch. The Japaneses only might be useful in this respect. My number (8) being so small, I hesitate to make a positive conclusion. Still the figures found here do not contradict WEISBACH.

I must emphasize that all weighings were done by myself and following the same method, viz. without pia and the ventricles being emptied. Since HARVEY 1) determined the average total volume of the ventricles to be 30.4 cM², the cerebral fluid would amount to a weight of almost 30.4 gr. Besides, this author found the largest brains to have the smallest ventricles, the smallest brains having the largest ventricles, the fluid increasing the T.B.W. in an inverse way.

The cerebellum was severed immediately above the emergence of the VII and VIII roots.

My results in the Dutch are recorded in the two following tables.

n,	٧	И	۵	23	
	u	Δ	6	**	٠

Origin	Further indication	T.B.W.	Weight cerebell.	0/0 Cer.	Age	Height	Causa mortis
W.G.	15256	1452 gr.	171.5	11.81 0/0	9 years	?	trauma
	15283	1680 .,	156	9.28 "	16 "	176 c.M.	91
Gron.	Gor.	1470	164	11.15 "	17 "	165 "	empyeem. pneum.
20	Boe	13601/2 .,	117.5	8.63 "	18 "	178 "	peritonitis
W.G.	15297	1299	137	10:54 "	26 "	170 "	t. b. p.
Gron.	Gro.	1375	128	9.30 "	42 "	160 "	ca. ventr.
31 ,	Verh.	1224 .,	136	11.11 "	<b>4</b> 5 "	170 "	ileus (perit.)
89	de H.	1401	143.5	10.24 "	62 "	181 "	carc. prostat.
**	Siem.	1102	115	10.43 "	74	168 "	nephr. chron.
	Hoog.	1054 .,	114	10.81 "	74 .,	165 "	carc. oesoph.
W.G.	15263	1365 "	145	10.62 "	75 "	170 "	carc. recti.
20	15243	1124 "	101	8.98 "	78 "	163 "	carc. linguae
	15271	12781/2	155	12.12 "	87 "	155	?
Average 1322 gr.		137.2	10.3780/0				

Hence we see that I found the average cerebellum weight in the Dutch to be 10,339 or shortly 10,4% of the total brain weight, a figure almost equal to that of MEYNERT and somewhat smaller than all the figures of WEISBACH. Of course, I do not conclude from my figures the cerebellum weight in the Dutch to be smaller than in the races examined by WEISBACH; I rather believe the ways of severing and weighing, used by the latter to be somewhat different from my method. It is evident

<sup>1)</sup> HARVEY, The volume of the ventricles of the brain. Anat. Record. Vol. V, 1911, pag. 304.

Women

Origin	Further Indica- tion	···		Weight cerebell.	<sup>0</sup> / <sub>0</sub> Cere- bell.		Age		Height		Causa mortis
Gron.	Krijthe <sup>1</sup> )	150 <b>2</b>	gr.	1371/2	9.15	0/0	4	years	113	c.M.	peritonit. (app.)
W.G.	15258	1369	**	1 <b>2</b> 5	9.17	**	25	.,	175	22	trauma
**	15244	1238	**	140	11.31	**	26	22	160	39	abortus
Gron.	Lenz	1103	**	117	10.60	21	28	23	145	93	anaemia
	Water	9961/2	20	1 <b>2</b> 6	12.64	**	31	22	151	99	29
99	Smed.	1291	20	139	10.76	**	58	99	154	25	carc. ovarii
**	Hamm.	1299	**	145	11.16	**	64	22	148	22	carc. ventric.
	Bekk.	1102	99	88	8.00	"	67	,99	157	20	vit. cordis
W.G.	15296	1087.5	25	125.75	11.56	"	71	27	159	22	t. b. p.
**	15310	1059	,,	112	10.57	,,	72	,,	155	21	nephr. chron.
20	15302	1210	29	136	11.24	.,	76	99	155	90	arterioscler.
*2	15244a	1265	**	123	9.72	20	80	pj.	155	99	scl. a. cor. cond.
Average 1210.15 gr.			126.2	10.42	0/0						

Total average percentage in men and women 10.399 0/0.

that the precautions in weighing of two different authors are never exactly the same. This is also the reason why for comparison with my Mongolian material I used Dutch brains, examined by myself and did not confine myself to figures found by others in Caucasian races. Duo cum faciunt idem, non est idem.

My results in 22 Chinese brains, examined in identically the same way as the Dutch brains, are the following:

Origin	Ξ.	Further indication	T. B. W.	Weight Cerebell.	0/0 Cer. T.B.W.
North-Chin.	₹'	Body No. 18	1090 gr.	128 gr.	11.74 %
23 29 -	ð	" " 15 .	1130 "	1151/2	10.22 "
29 19	· 8	Autopsy 0949	1135 "*	124	10.92 "
20 99	~ 3 <sup>1</sup>	Body No. 7	1256 "	1391/2	. 11.10 "
99 99	ð	28	1277	110 "	8.61 "
	₹	11	1342 "	128 .,	9.53 "
10 20	ð	., ., 21	1 <del>4</del> 68 "	146	9.94 "

<sup>1)</sup> This cerebrum shows a "corpus ponto-bulbare".

Origin	Further indication	T. B. W.	Weight Cereb.	<sup>0</sup> / <sub>0</sub> Cerebellum
Chin. fr. D. EIndia	Nº. 11	1014 gr.	124 gr.	12.22 %
80 80 PP	., 9	1076 "	109 "	10.10 "
20 00 00	" 3	1120 "	116	10.34 "
	., 17	1085 "	1151/2 "	10.64 "
* 1 2	14	1170	. 130 "	11.11 "
90 90 99	· " 2	1161 "	131 "	11.30 "
00 00 00	,, 8	1171	129 "	11.01 "
50 00 10	" <del>1</del>	1195 "	116	9.70 "
20 20 29	., 1	1228 "	143 "	11.60 "
., .,	<b>"</b> 5	1261	141 "	11.18 "
** 99 **	7	1295 "	130 "	10.04
00 00 00	6	1261 "	116 "	9.20 "
20 20 20	15	1271	122 "	9.60 "
	, 10	1344 "	134 "	9.97 "
99 99 99	12	1425 "	135 "	9.47 "
Average		1217 gr.	126.5 gr.	10.39 %

In addition I give the figures found with 8 Japanese brains for which material I am greatly indebted to Prof. G. Fuse of Sendai.

Averag	Average		her ition	T.B.W.		Weight Cerebellum		<sup>0</sup> / <sub>0</sub> Cere- bellum		Age		Height		C.M.
Japanese	8	Nº.	1	1284	gr.	1391/2	gr.	10.86	0/0	27	years	146	cM.	vit. c.
**	••	,,	2	1239	м	1231/2	11	9.96	12	28	10	163	**	t. b. p.
**	**	**	3	10611/2	10	117		11.02	**	21	••	154		PD DD DD
**	,,	**	4	1296	99	1381/2	**	10.68	**	28	**	160	**	99 SS SS
**	**	,,	5	1188	**	113	**	9.51	200	26	**	153		nephr.
**	**	**	6	1214	**	119		9.80	**	36	**	153	10	carc. v.
**	**	,,	7	1218	••	1221/2	**	10.05	**	36	**	156	**	t. b. p.
H .	**	**	8	1198	**	134	٠,	11.25	**	21	**	146	**	19 99 90
Averag	ge			1212.3	1 gr.	125.9	gr.	10.38	3 <sup>0</sup> / <sub>0</sub>					

The relative cerebellum weight in my Chinese (and Japanese) differs so little from the Dutch, that I hesitate to draw a conclusion. A much larger number of brains would be necessary to ascertain such a conclusion.

I think myself qualified though in assuming the relative cerebellum weight in the Chinese to be practically equal to that of the Dutch. If any difference exists, the weight is *perhaps slightly less* in the Chinese, especially in the Northern Chinese.

It is certainly noteworthy that in the tables of WEISBACH the Magyars show a slightly smaller cerebellumpercentage than the other races of the former Austro-Hungarian monarchy. This is interesting on account of the fact that the Magyars are generally considered as a largely Mongolian race and that also these weighings were done by the same.

As mentioned at the beginning, TOPINARD on account of CLAPHAM's work thinks himself qualified to conclude the cerebellumpercentage in the Chinese to be considerably smaller than in Caucasian races.

CLAPHAM himself in this article does not make this conclusion, publishing only the figures of the total brain weight in his 16 cases and the weight of the cerebellum connected with pons and medulla oblongata.

Now there are two methods of using the latter figures for our purpose. Both methods include a source of errors.

The first method is calculating the cerebellum weight from the figures for the cerebellum, pons and medulla oblongata, given by CLAPHAM using the statistics made in Europe, the average weight of the human oblongata + pons being, according to BOYD,  $1,8\,^0/_0$  of the T. B. W. (according to CRICHTON BROWNE l.c.  $1,9\,^0/_0$ , to REY  $1,99\,^0/_0$ ). A weak point in this method is our ignoring if it avails with the same average of  $1,8\,^0/_0-1,9\,^0/_0$  for the Chinese also. (I had no pleasure in mutilating my material for controlling this).

A second method is, taking also in Europeans, instead of the cerebellum weight, the weight of cerebellum + pons and oblongata and comparing this weight (which we may call the *metencephalic weight*) with CLAPHAM's results in the Chinese.

In the next table I used both methods reducing to grammes the avoir du poids figures of CLAPHAM.

From this appears that on account of the first calculation TOPINARD is right in concluding from the figures of CLAPHAM the average cerebellumpercentage of his 16 cases to be less than in Europeans, the average in the cases of CLAPHAM being even less than  $10\,^{\rm o}/_{\rm o}$ .

Doubting this method of calculating the cerebellum weight from the weight of cerebellum, pons and oblongata to be trustworthy, we may compare the figures, found by CLAPHAM for the whole metencephalon with those found in the English by THURNAM 1).

<sup>1)</sup> THURNAM. On the weight of the brain and on the circumstances affecting it. Journ. of Mental science. Vol. XII, 1866, p. 1.

Hongkong N <sup>0</sup> .	T. B. W.	Metenc. Weight	Metenc. 0/0	Cereb. Weight	Cereb. 0/0	Sex	Age (approx.)
1	1410.3 gr.	177.2 gr.	13.56.0/0	151.8 gr.	10.77 0/0	ď	30 years
. 2	1417.4 "	163.0 "	11.5 "	137.5 "	9.7 "	8	28 "
3	1516.7 "	156.0 "	10.28 "	128.7	8.4 "	8	45 "
4	1587.5 "	184.2 .,	11.61 "	155.5 "	9.8 "	8	40
5	1410.3 "	170.0 "	12.06 "	151.8 "	10.7 "	ď	50 "
6	1360.0 "	138.0 "	10.94 "	111.5 "	8.2 "	· 8	40
7	1318.0 "	156.0 ,.	11.83 "	132.3 "	10.05 "	ð	25
8	1530.0 "	187.0 "	12.50 "	159.5 "	10.42 "	8	48
9 -	1403.3 "	170.0 "	12.12 "	144.8 "	10.32 "	ð	55
10	1467.5 "	175.9 "	12.06 "	149.5 "	10.60 "	8	35 "
11	1311.0 "	138.0 "	11.11 "	114.5 "	8.7 "	·3 <sup>*</sup>	30 "
12	1289.0 ,	170.0 "	13.18 "	146.8 "	11.4 "	2	26 "
13	1389.0 "	156.0 "	11.22 "	131.0 "	9.43 "	\$	38 "
14	1247.0 "	138.0 .,	11.93 "	115.6 "	9.27 "	2	30 "
15	1204.8 ,,	156.8 "	12.82 "	134.3 "	11.10 "	ę.	70 "
16	1311.0 "	156.0 "	11.89 "	132 4	1010 .,	\$	18 "
Average	1385.8 gr.		11.91 0/0	137.4 gr.	9.91 %		

On account of 470 weighings (257 men and 213 women) THURNAM determined the metencephalic percentage to be  $12.9^{\circ}/_{0}$  in men and  $13.1^{\circ}/_{0}$  in women: total average  $13.0^{\circ}/_{0}$ .

Now the total metencephalic percentage found by CLAPHAM is  $11.91 \, ^{\rm o}/_{\rm o}$ , so that also this figure would be smaller in the Chinese.

Still we have to be very careful with CLAPHAM's figures.

In the very meeting in which CLAPHAM communicated his results, DISTANT observed the T.B.W. figures of CLAPHAM to be exceedingly high and to exceed even those given by BARNARD DAVIS for the average skullcapacity of the Chinese.

Though the average capacity mentioned by BARNARD DAVIS 1) for the male Chinese skull (47,87 ounces or 1357 cM.2) may be too small, DISTANT'S criticism keeps its value even considering the average skull

<sup>1)</sup> BARNARD DAVIS. Thesaurus craniorum. Catalogue of the skulls of various races of man. London 1867 and the supplement on this work, edited in 1875. I regret this work not to be at my disposal.

capacity to be 1456 cM.<sup>2</sup> as found by HABERER <sup>1</sup>) in 28 men from Peking.

The relation between skullcapacity and brain weight with pia and ventricular fluid determined by Welcker 2) for this category amounts to 93  $^{0}$ /<sub>0</sub>. Bolk 3) found in 40 years old Dutchmen figures varying from 90 to 96.5  $^{0}$ /<sub>0</sub>, Manouvrier 4) however in the French only 87  $^{0}$ /<sub>0</sub>.

Taking the relation to be  $92\,^0/_0$ , we should expect with an average male skull-capacity of 1456 cM² a brain weight of 1380 gr. with ventricular fluid and pia. Substracting for the latter two 30.4 + 53.6 = 83.5 gr., we keep as netto brain weight 1296.5 gr. 5) (in a relation of  $90^0/_0 \pm 1275$  gr., in a relation of  $87^0/_0:1240$  gr.).

In my 7 Northern-Chinese I found the average netto brain weight to be 1243 gr. whereas CLAPHAM in his Southern-Chinese — who according to my experience have a smaller average T.B. W. than the Northern-Chinese, stated the average male brain weight to be 1430 grammes!

In my opinion we should be very careful with CLAPHAM's figures. Apparently TOPINARD himself doubts the total weight figures mentioned by this author saying (l.c. p. 57) "La moyenne (des poids de l'encephale) des Chinois de CR. CLAPHAM a étonné tout le monde. Nous attendrons avant d'en tirer une conclusion".

Moreover we are confirmed in presuming CLAPHAM to have made errors in his weighings by the equally low percentage he found in two Pelewnatives and one Hindoo, published in the same article.

As appears from my tables the cerebellar percentage found in the Chinese varies from  $8.61^{\circ}/_{0}$  to  $12.22^{\circ}/_{0}$ , in the Dutch from  $8.00^{\circ}/_{0}$  to  $12.12^{\circ}/_{0}$ .

So the variation in the cerebellar percentage is about  $4^{0}/_{0}$ , in the Chinese as well as in the Dutch.

As mentioned above, WEISBACH also found large variations and is inclined to correlate this among other things with the length of the body, the increase of which should influence more the cerebellum than the forebrain.

Having at my disposal not enough human cerebra of individuals whose body length was noted 6), I have tried to consider this problem by

<sup>&</sup>lt;sup>1</sup>) HABERER. Schädel und Skeletteile aus Peking. Verlag von Gustav Fischer. Jena 1902 (p. 69).

<sup>&</sup>lt;sup>2</sup>) WELCKER. Die Kapazität und die drei Hauptdurchmesser der Schädelkapsel bei den verschiedenen Nationen. Arch. f. Anthropologie. Bnd. 16. 1886.

<sup>&</sup>lt;sup>3)</sup> BOLK. Beziehungen zwischen Hirnvolum und Schädelkapazität, nebst Bemerkungen über das Hirngewicht der Holländer. Petrus Camper. Vol. II, 1902.

<sup>4)</sup> MANOUVRIER. Sur l'indice cubique du crâne. Comptes rendus de l'association française pour l'avancement des sciences. Congrès Reims 1880. Quoted after MARTIN. Allgemeine Anthropologie.

<sup>5)</sup> According to HARVEY (l. c.), the average weight of the ventricular fluid is 30.4 gr. while according to REY (l. c.) the average weight of the pia (wet) is 53.06 gr.

<sup>6)</sup> In the Dutch I found up to 160 c.M. a larger average than in 160 c.M. and more, but in my Japanese the average does not conflict with this conception.

determining cerebellumpercentages in mammals of the same order but of different size 1).

Order	Species	T. B. W.	Weight Cer.	<sup>0</sup> / <sub>0</sub> Cerebellum	Fixation
Marsupialia	Didelphys m Macropus r.	6.17 gr. 55.00 "	0.87 gr. 7.70 "	14 <sup>0</sup> / <sub>0</sub>	formal.
Rodentia	Mus dec. 2) Lepus can. 2)	_	0.25 gr. 1.35 "	13 º/ <sub>0</sub> 15 "	fresh
Insectivora	Talpa eur. <sup>2</sup> ) Erinaceus <sup>2</sup> )	- -	0.17 gr. 0.39 "	13 º/ <sub>0</sub> 11 ,,	fresh 
Ungulata Perissodact	Tapirus ind. Equus cab.	265.00 gr. 468.00 "	35.00 gr. 58.50 "	13.2 º/ <sub>0</sub> 12.5 "	formal.
Artiodact	Tragulus juv. Oreas liv.	16.80 " 192.00 "	1.8	10.7 " 9.4 "	00
Proboscidea	Elephas indic.	3860.00 gr.	940.00 gr.	24.3 %	formal.
Сеtaceн	Phocaena com. Balaenopt. Sibb.	390.00 gr. 5676.0 "	58.00 gr.	15.0 º/ <sub>0</sub> 18.95 "	formal.
Carnivora	Felis dom.	23.05 gr.	3.5 gr.	13.66 %	formal.
Felidae Canidae	Felis leo Felis tigris Vulpes lagopus Canis fam. box.	197.5 208.2 28.15 73.7	21.0 21.6 3.55 6.0	10.60 " 10.36 " 12.6 " 8.9 "	99 29 90
Edentata	Choloepus did.	34.0 gr.	6.1 gr.	17.6 %	formal.
Simiae	Hapale ros. 3) Callithrix py. Semnopith. ceph. Macacus rh. Hylobates synd. Simia satyrus	42.3 gr. 65.0 ,, 70.0 ,, 105.0 ,, 293.0 ,,	0.62 gr. 4.8 " 8.0 " 6.3 " 14.0 "	7.8 % % % % % % % % % % % % % % % % % % %	fresh? formal.

<sup>1)</sup> These four figures are taken from Ziehen (Bardeleben's Handbuch der Anatomie).

<sup>&</sup>lt;sup>2</sup>) This figure is taken from FLATAU und JACOBSOHN's Handbuch der Vergl. Anatomie des Centr. Nervensystems. 1899.

<sup>3)</sup> These weighings were also done without pia, the ventricles being emptied and the brain was cut off near the calamus.

The animals in this list are so arranged that the smallest specimen of the order is always placed ahead.

Comparing in this list the large animals and the small ones of the same order, we see in some groups (Rodents, Cetacea, Simiae) the largest representants to have a larger cerebellumpercentage per T.B.W.

This, however, is not always, even not mostly so, especially not in Insectivores, Ungulates and Carnivores (Felides), and while the Whale and Elephant — two exceedingly large animals of different orders — indeed show an enormous relative cerebellum weight, I found on the other hand the small Choloepus didactylus having the very considerable figure of  $17.6^{\circ}$ <sub>0</sub>.

Without doubt other factors than body size influence this relation and in a larger degree even than the latter. The most important factor appears to be the habit of life, especially the manner of moving and the peculiar use of the limbs for moving and grasping.

So, concerning the remarkable contrast between the two Insectivores, probably the very different way of life of these two representants causes the cerebellum of Talpa to be relatively somewhat smaller than in Erinaceus. Overlooking an eventual difference in favour of the forebrain in the hedgehog 1) the larger cerebellumpercentage in the mole may be explained by the movement of the extremities of the latter. This animal is a very sturdy worker, who in his continually digging life, uses his extremities very much, strongly and exactly. Its feet, especially the forefeet, are not only locomotor organs, but also digging instruments, much more so than in Erinaceus.

That special functions of the limbs exercise a large influence on the weight of the cerebellum — especially of the hemispheres — also results from the high percentage of the cerebellum in the Sloth (Choloepus didactylus), an animal that moves extremely slow and prudently and, by the pending posture in which it finds its way in the trees, lays great claims on the innervation of its extremities.

Whereas in the gait of most Quadrupeds bilateral symmetric innervation acts the largest part, in this pending movement in trees slow, unilateral motions and consequently antagonistic innervation of the limbs are of utmost importance. This motion is much more complicated than the simple, rhytmic, bilateral motion, as e.g. in Ungulates.

In my opinion the large size of the cerebellum in the Sloth may be alleged in favour of the idea of Leiri<sup>2</sup>) that the hemispheres of the cerebellum are connected especially with inhibition of motions by inner-

<sup>1)</sup> Talpa is blind, Erinaceus is not.

<sup>2)</sup> LEIRI. Le cervelet un organe servant à l'innervation des antagonistes dans l'activité musculaire. Acta Oto-laryngologica, Vol. VI. Fasc. 3-4, p. 516.

LEIRI's conception agrees very well with INGVAR's conclusions and seems to explain very well the symptoms, described by BABINSKI, VAN RIJNBERK, BARANY and GORDON HOLMES and others in cerebellar insufficiency.

vation of antagonists since it is supposed that in quick motions the antagonists are activated chiefly in the end of the motion, whereas in slow, searching motions they are acting nearly continually (WAGNER 1)).

In still another way my table shows the influence of the function of the extremities on the relative size of the cerebellum.

So the Whale, whose body and T.B.W. are much larger than those of the Elephant nevertheless has a smaller cerebellumpercentage than the Elephant. This difference is certainly due to the poor development of the extremities in the Whale and the exceedingly fine motility (also unilateral) of the Elephants limbs and trumpet.

Consequently we find, for the relative cerebellumweight, the motile capacities, not the size of the animal to be the main point.

These facts confirm BOLK's conception of the great significance of the extremities, especially their asymmetric unilateral movements for the development of the hemispheres of the cerebellum, a thesis confirmed by the experiments of VAN RIJNBERK and his collaborators, further by Thomas and Durupt and even by Gordon Holmes, who for the rest does not agree with BOLK's theory of cerebellar localisation.

That, however, in some cases the cerebellumpercentage increases indeed in larger animals of the same order, is seen in Sharks, where the cerebellum, not or hardly fissurated in the smaller representants 2), shows a large amount of transverse convolutions in the larger specimens of this class. In the larger sharks the greater increase of the cerebellum may thus be demonstrated even ad oculos although it may be expressed in figures also:

Name	T. W. B.	Weight cer.	Cereb. 0/0	
Scyllium can. 3)	666 mgr.	96.5 m.gr.	14.5 %	
Galeus canis	8750 "	1390 "	15.9 "	
Lamna cornub.	17110 "	3580 "	20.9 "	

Though in some sharks which have a different way of moving than the ordinary ones (f.i. Angelus Squatina) also contrary relations may occur, the relative increase of the cerebellum compared to the cerebrum in larger specimens is not surprising, the development of the corpus cerebelli being largely a function of the musculo-sensory system of all parts of the body, whereas the development of the forebrain in these animals depends almost wholly on the sense of smell. So also the forebrain in mammals contains areas (smell, vision, hearing), the development

<sup>1)</sup> R. WAGNER. Ueber die Zusammenarbeit der Antagonisten bei der Willkürbewegung, 1ste Mitt. Zeitschr. f. Biologie, Bnd. 83, 1925, p. 59; 2te Mitt. ibid, p. 120.

<sup>2)</sup> Confer ARIENS KAPPERS. Vergleich. Anatomie des Nervensystems. Part II, pag. 647 and VOORHOEVE, Het Cerebellum der Plagiostomen. Dissertatie. Amsterdam, 1914.

<sup>3)</sup> These figures are the average of three weighings.

of which neither is a function of the body. In the cerebellum of fishes this would avail only for the auriculus, the development of which does not depend on impulses of the spino- and olivo-cerebellar systems (pontocerebellar systems do not yet exist in fishes), but on the NN. laterales (and N. VIII).

So in some bonyfishes where the N. lateralis is very large (Mormyrus) the cerebellum increases enormously by the huge development of the auriculi and the associated valvula.

Finally I would like to point out that a determination of the relation between cerebellum weight and body weight and between cerebellum weight and the weight of the spinal cord without doubt will cast more light on this subject.

Mathematics. — "Ein algebraisches Kriterium für die Lösbarkeit eines Systems homogener Gleichungen." By B. L. VAN DER WAERDEN. (Communicated by Prof. R. WEITZENBÖCK.)

(Communicated at the meeting of November 28, 1925.)

Die allgemeine Theorie der Elimination gestattet es, für jedes Gleichungssystem

$$\begin{cases}
f_1(x_1,\ldots,x_n)=0 \\
\vdots \\
f_r(x_1,\ldots,x_n)=0
\end{cases}$$

zu entscheiden, ob das System Lösungen in einem gegebenen algebraischabgeschlossenen Körper 1) hat, und wenn ja, diese Lösungen zu bestimmen. Ein algebraisches Kriterium, in Sinne eines Systems algebraischer Relationen zwischen den Koeffizienten der Polynome  $f_1, \ldots, f_r$ , deren Erfülltsein entscheidend ist für die Lösbarkeit, gibt sie aber nicht, und kann sie nicht geben, da ein solches Kriterium unmöglich ist. Das ist leicht zu sehen im Spezialfall r=n+1; in diesem Fall gibt das Verschwinden der Resultante eine notwendige und "im allgemeinen" hinreichende Bedingung, aber die Resultante verschwindet auch dann noch, wenn die Lösung "ins Unendliche rückt".

Diese Schwierigkeit kann nun dadurch gehoben werden, dass man die Polynome  $f_1, \ldots, f_r$  homogen in  $x_1, \ldots, x_n$  voraussetzt. Die Gleichungen (1) haben dann (wenn keine der Gradzahlen von  $f_1, \ldots, f_r$  gleich Null ist) immer die Nulllösung  $x_1 = 0, \ldots, x_n = 0$ . Die Bedingung dafür, dass sie ausserdem noch mindestens eine Lösung haben (und dann zugleich eine Schar proportionaler Lösungen) kann durch algebraische Gleichungen in den Koeffizienten ausgedrückt werden, was im Falle r = n aus der Theorie der Resultante bekannt ist 2) und hier allgemein gezeigt werden soll (§ 3).

Es stellt sich dabei heraus, dass, wenn man auf explizite Hinschreibung

Der MERTENSsche Beweis gilt nicht bei beliebigen Koeffizientenkörper, sondern nur wenn dieser Körper den der rationalen Zahlen umfasst (Körper der Charakteristik Null in der STEINITZschen Bezeichnungsweise).

<sup>1)</sup> Vgl. § 2, Satz 1.

<sup>&</sup>lt;sup>2</sup>) Siehe etwa F. S. MACAULAY, Modular Systems, Cambridge Tracts 19 (1916) S. 13; oder F. MERTENS, Sitzungsber. Wien 108 (1899) S. 1176 und 1386. Der Beweis, dass das Verschwinden der Resultante hinreichend ist für die Existenz einer von der Nulllösung verschiedenen Lösung ist bei MACAULAY erst dann vollständig, wenn man den Satz auf S. 67, Zeile 4, hinzunimmt. Verschwindet nämlich die Resultante, so hat die aus den Formen vom Grade l+1 gebildete Matrix nicht den maximalen Rang, also gibt es eine Idealgleichung vom Grade l+1, also hat das Ideal  $(F_1, \ldots, F_n)$  nach dem genannten Satz einen Rang n0, also gibt es eine von 0 verschiedene Nullstelle.

der algebraischen Bedingungen verzichtet, und sich mit der Erkenntniss der Existenz begnügt, der genannte Satz eine fast unmittelbare Folge von zwei fundamentalen HILBERTschen Sätzen ist, welche als HILBERTscher Nullstellensatz und HILBERTscher Basissatz bezeichnet werden mögen. Neben diesen Hauptsätzen der Idealtheorie wird nur noch der Steinitzsche Haupsatz der Körpertheorie (vgl. § 2) benutzt werden.

Die Theorie wird sodann durch "sukzessive Elimination" auf den Fall ausgedehnt werden, wo die Gleichungen (1) mehrfachhomogen sind, etwa homogen in  $x_1, \ldots, x_m$ , in  $y_1, \ldots, y_n$ , u.s.w. Auch hier ergeben sich algebraische Bedingungen dafür, dass eine nicht in den trivialen Lösungssystemen  $x_1 = \ldots = x_m = 0$  oder  $y_1 = \ldots = y_n = 0$  u.s.w. enthaltene Lösung existiert (§ 4).

Alle Beweise gelten bei beliebigem Koeffizientenkörper, wenn nur die Lösungen einem algebraisch-abgeschlossenen Erweiterungskörper (vgl. § 2) entnommen werden.

Die Ergebnisse gestatten viele Anwendungen. So ergeben sie ohne Weiteres die Verallgemeinerung auf beliebige Koeffizientenkörper eines von E. FISCHER gegebenen, auf Eliminationstheorie beruhenden, Beweises eines E. NOETHERschen Satzes, der die Existenz eines algebraischen Kriteriums für "absolute Irreduzibilität" einer Form, d.h. Irreduzibilität in Bezug auf jeden algebraischen Erweiterungskörper des Koeffizientenkörpers, besagt<sup>3</sup>).

Auch ermöglicht die Theorie eine algebraische Bestimmung der Lösungen des Systems (1) für den Fall, dass endlichviele Klassen proportionaler Lösungen vorhanden sind, entsprechend der bekannten Lösung von Gleichungen mit Hilfe der Resultante im Falle von n-1 homogenen Gleichungen in n Unbestimmten. Es wird nämlich die Existenz eines Polynoms in gewissen Unbestimmten  $u_{ij\ldots k}$ , gezeigt werden, welches die u-Resultante des Gleichungssystems heisst, und dessen lineare Faktoren die Lösungsklassen rational bestimmen (§ 5). Im Fall von n-1 homogenen Gleichungen in n Unbestimmten ist die u-Resultante einfach die Resultante der n-1 gegebenen Formen und einer Linearform  $u_x$  mit unbestimmten Koeffizienten. Die Methode, die im Fall endlichvieler Lösungsklassen zur u-Resultante führt, lässt sich, wie im § 5 nur kurz angedeutet werden soll, ausdehnen auf den allgemeinen Fall einer algebraischen Mannigfaltigkeit von Lösungsklassen.

Auf andere Anwendungen, insbesondere auf die Theorie der algebraischen Funktionen von *n* veränderlichen, sowie auf die Begründung der abzählenden Geometrie, gedenke ich an anderer Stelle einzugehen.

# § 2. Definitionen und Hilfssätze.

Sei P ein Körper,  $P[x_1, \ldots, x_n]$  der Ring der Polynome in  $x_1, \ldots, x_n$  mit Koeffizienten aus P.

<sup>&</sup>lt;sup>3</sup>) E. NOETHER, Ein algebraisches Kriterium für absolute Irreduzibilität, Math. Ann. 85 (1922) S. 26; E. FISCHER, Math. Ann. 94 (1925) S. 163.

Wir stützen uns auf die folgenden, als bekannt vorausgesetzten, Definitionen und Sätze:

- 1. Man kann jeden Körper P algebraisch erweitern zu einem algebraisch-abgeschlossenen Körper, d.h. zu einem solchen, in welchem jedes Polynom einer Variabeln z in Linearfaktoren zerfällt  $^4$ ). Dieser Erweiterungskörper sei mit  $\Omega$  bezeichnet.
- 2. Sind  $f_1, \ldots, f_r$  Polynome eines gegebenen Polynombereichs, so ist das  $Ideal\ (f_1, \ldots, f_r)$  die Menge aller Polynome, die in der Gestalt  $\sum_{i=1}^r a_i f_i$ , wo  $a_1, \ldots, a_r$  beliebige Polynome des Bereichs sind, darstellbar sind.
- 3. Nullstellen des Ideals  $(f_1, \ldots, f_r)$  sind Elementsysteme  $\{\xi_1, \ldots, \xi_n\}$  eines Erweiterungskörpers von P, so dass  $f_1, \ldots, f_r$  (und folglich alle Elemente des Ideals) verschwinden, wenn man jedes  $x_i$  durch  $\xi_i$  ersetzt.
- 4. Hat ein Ideal  $(f_1, \ldots, f_r)$  in  $\Omega$  nur die Nullstelle  $\{0, \ldots, 0\}$ , so gibt es eine Zahl s, so dass alle Potenzprodukte s-ten Grades der Unbestimmten  $x_1, \ldots, x_n$ , dem Ideal angehören. Dieser Satz ist ein Spezialfall des Hilbertschen Nullstellensatzes  $^5$ ).
- 5. Gehört umgekehrt für irgendeinen Wert von s jedes Potenzprodukt s-ten Grades der Unbestimmten  $x_1, \ldots, x_n$  dem Ideal  $(f_1, \ldots, f_r)$  an, so hat das Ideal nur die Nullstelle  $\{0, \ldots, 0\}$  in  $\Omega$ .

(Denn in einer Nullstelle müssen alle Elemente des Ideals, also insbesondere die Elemente  $x_1^s, \ldots, x_n^s$ , verschwinden).

- 6. Ein H-Ideal ist ein Ideal, dessen Basis aus homogenen Polynomen (Formen) besteht.
- 7. Ist  $(f_1, \ldots, f_r)$  ein H-Ideal, sind  $l_1, \ldots, l_r$  die Gradzahlen der Formen  $f_1, \ldots, f_r$ , und bildet man für einen beliebigen Wert von s die Formen  $g_1, \ldots, g_t$  s-ten Grades, die aus  $f_1, \ldots, f_r$  entstehen indem man  $f_i$  mit allen Potenzprodukten vom Grade s- $l_i$ , der Unbestimmten  $x_1, \ldots, x_n$  multipliziert (wenn solche existieren, also wenn  $s > l_i$ ), so ist jede Form s-ten Grades des Ideals von diesen Formen  $g_1, \ldots, g_t$  linear-abhängig. Die Koeffizientenmatrix dieser Formen heisst die dialytische Matrix des Ideals  $(f_1, \ldots, f_s)$  für den Grad s  $^6$ ).
- 8. Hilbertscher Basissatz für ganzzahlige Polynome<sup>7</sup>). Eine beliebige Menge von ganzzahligen Polynomen enthält eine endliche Untermenge  $f_1, \ldots, f_r$ , so dass die gegebene Menge ganz im Ideal  $(f_1, \ldots, f_r)$  (Ideal im Sinne des ganzzahligen Polynombereichs) enthalten ist.

<sup>4)</sup> E. STEINITZ, Algebraische Theorie der Körper. J. f. M. 137 (1910) pag. 279 (§ 12).
5) D. HILBERT, Ein allgemeines Theorem über algebraische Formen, Math. Ann. 42 (1893) S. 473 (§ 3 der Arbeit "Ueber die vollen Invariantensysteme"). HILBERT setzt voraus, dass Ω der Körper der komplexen Zahlen ist; der Beweis gilt aber allgemein, und benutzt nur die binäre Eliminationstheorie, welche, etwa in der bekannten EULERschen Fassung, ganz allgemeingültig ist. Für einen anderen, nur auf Körpertheorie und Idealtheorie beruhenden, Beweis siehe meine demnächst in Math. Ann. erscheinende Arbeit "Zur Nullstellentheorie Polynomideale".

<sup>6)</sup> F. S. MACAULAY, a. a. O., S. 64.

<sup>7)</sup> D. HILBERT, Ueber die Theorie der algebraischen Formen, Math. Ann. 36 (1893) p. 473.

#### § 3. Der Hauptsatz.

Die Anzahl der Potenzprodukte vom Grade s der Unbestimmten  $x_1, \ldots, x_n$  ist bekanntlich gleich

$$\omega_s = \binom{s+n-1}{s}.$$

Mit Hilfe von 7. kann man die Sätze 4. und 5. als Sätze über Matrizen aussprechen:

9. Hat das H-Ideal  $(f_1, \ldots, f_r)$  nur die Nullstelle  $\{0, \ldots, 0\}$  in  $\Omega$ , so gibt es eine Zahl s, so dass die dialytische Matrix des Ideals für den Grad s den rang  $\omega_s$  hat, und umgekehrt.

Seien nun  $F_1, \ldots, F_r$  Formen der gleichen Gradzahlen wie  $f_1, \ldots, f_r$ . mit unbestimmten Koeffizienten  $a_1, \ldots, a_p$ . Sind dann  $a_1, \ldots, a_p$  die Koeffizienten von  $f_1, \ldots, f_r$ , so entsteht  $f_i$  durch die Spezialisierung  $a \rightarrow a$  aus  $F_i$ . Seien  $b_{s1}(a), \ldots, b_{s\rho_s}(a)$  die  $\omega_s$ -reihigen Unterdeterminanten der dialytischen Matrix von  $(F_1, \ldots, F_r)$  fur den Grad s, als ganzzahlige Polynome in  $a_1, \ldots, a_p$  geschrieben. Wenn für ein s solche nicht vorhanden sind, so setzen wir  $\varrho_s = 1$ ,  $b_{s1}(a) = 0$ . Dann sind  $b_{s1}(a), \ldots, b_{s\rho_s}(a)$  die Unterdeterminanten der dialytischen Matrix von  $(f_1, \ldots, f_r)$ , und aus g. folgt:

10. Das H-Ideal  $(f_1, \ldots, f_r)$  hat dann und nur dann eine von  $\{0, \ldots, 0\}$  verschiedene Nullstelle in  $\Omega$ , wenn für alle Werte von s und k ( $k \leq \varrho_s$ ):

Nach 8. enthält die Reihe des ganzzahligen Polynome  $b_{11}, \ldots, b_{1\rho_1}, b_{21}, \ldots$  eine eindliche Untermenge  $b_{\varepsilon\xi}, b_{\eta\theta}(a), \ldots$ , so dass die ganze Formenreihe im Ideal  $(b_{\varepsilon\xi}(a), b_{\eta\theta}(a), \ldots)$  enthalten ist. Diese Untermenge kann man zu einem Abschnitt  $b_{11}(a), \ldots, b_{1\rho}(a), \ldots, b_{\sigma_1}(a), \ldots, b_{\sigma_1\rho_2}(a)$  ergänzen, ohne dass die genannte Eigenschaft verloren geht. Diesen Abschnitt kann man eindeutig bestimmen durch die Forderung, dass er der kleinste Abschnitt mit der genannten Eigenschaft sein soll. Es folgt, dass das unendliche Gleichungssystem (2) dem endlichen Gleichungssystem

$$b_{11}(a) = 0, \ldots, b_{1\rho_1}(a) = 0$$
  
 $b_{\sigma 1}(a) = 0, \ldots, b_{\sigma \rho_{\sigma}}(a) = 0$ 

äquivalent ist. Bezeichnet man die Polynome  $b_{11}$  (a), ...,  $b_{\tau\rho_{\sigma}}$  (a) kurz mit  $b_1$  (a), ...,  $b_t$  (a), nennt ihre Gesamtheit das Resultantensystem der Formen  $F_1, \ldots, F_r$ , und versteht unter dem Resultantensystem des spezialisierten Formensystems  $f_1, \ldots, f_r$  die Gesamtheit der spezialisierten Polynome  $b_1$  (a), ...,  $b_t$  (a), so kann man den Hauptsatz in der folgenden Form aussprechen:

11. Die notwendige und hinreichende Bedingung dafür, dass die Formen  $f_1, \ldots, f_r$  eine von  $\{0, \ldots, 0\}$  verschiedene gemeinsame Nullstelle in  $\Omega$  haben, ist gegeben im Verschwinden ihres Resultantensystems.

Es sei bemerkt, dass die Polynome  $b_1(a) \dots, b_t(a)$  homogen in den Koeffizienten jeder einzelnen Form  $F_k$  sind.

Mit 11. ist das gestellte Problem gelöst. Es mögen aber noch einige mit dem Resultantensystem zusammenhängende Sätze Platz finden.

12. Ist  $b_{\lambda}$  (a) ein Polynom des Resultantensystems der Formen  $F_1,...,F_r$ , und  $x_k$  einer der Unbestimmten, so ist

$$x_k^{\sigma} b_{\lambda} (a) \equiv 0 (F_1, \ldots, F_r)$$

im ganzzahligen Polynombereich der  $a_i$  und  $x_k$ . Beweis. Sei

$$b_{\lambda}(a) = b_{si}(a)$$
  $(i \leq \varrho_s).$ 

 $b_{si}(a)$  ist entweder Null, oder eine Determinante aus den Koeffizienten einer Untermenge, etwa  $G_1, \ldots, G\omega_t$ , der Formen  $G_1, \ldots, G_t$ , welche aus  $F_1, \ldots, F_r$  in der Weise, wie es im § 1 (Satz 7) angegeben ist, gebildet werden. Sei

$$G_{1} = a_{11} u_{1} + \ldots + a_{1\omega_{s}} u_{\omega_{s}}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$G_{\omega_{s}} = a_{\omega_{s}1} u_{1} + \ldots + a_{\omega_{s}\omega_{s}} u_{\omega_{s}}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

wo  $u_1, \ldots, u_{\omega_s}$  die Potenzprodukte s-ten Grades der Unbestimmte  $x_1, \ldots, x_n$  sind. Unter diesen befindet sich  $x_k^s$ ; löst man (3) nach  $x_k^s$  auf, so findet man nach bekannten Determinantensätzen:

$$x_k^s b_{si}(a) \equiv 0 (G_1, \ldots, G_{\omega_s})$$
  
 $\equiv 0 (F_1, \ldots, F_r),$ 

folglich, da  $s \leq \sigma$  und  $b_{si} = b_{\lambda}$ ,

$$x_k^{\sigma} b_{\lambda}$$
 (a)  $\equiv 0 (F_1, \ldots, F_r)$ , q.e.d.

Die Gesamtheit der ganzzahligen Polynome c (a), für die eine Kongruenz

in ganzzahligem Polynombereich der a und x stattfindet, ist nach MERTENS  $^{8}$ ) von Index k unabhängig, und stellt ein Primideal dar (d.h. eine Menge von Polynomen, zu der mit f und g immer f+g und f-g, mit f immer a f, wo a ein beliebiges Polynom ist, und mit f g immer entweder f oder g gehört), welches I heissen soll.

13. Alle Polynome von I haben die Eigenschaft, für a = a zu verschwinden wenn die Formen  $f_1, \ldots, f_r$  eine von  $\{0, \ldots, 0\}$  verschiedene gemeinsame Nullstelle  $\{\xi_1, \ldots, \xi_n\}$  haben.

<sup>8)</sup> F. MERTENS, Zur Theorie der Elimination, Sitzungsber. Wien 108 (1899) pag. 1174. Der MERTENSsche Beweis gilt sowohl für den Polynombereich  $P[a_1, \ldots, a_p, x_1, \ldots, x_n]$ , als für den ganzzahligen Polynom-bereich der  $a_1, \ldots, x_k$ .

Das folgt unmittelbar aus der Kongruenz (4) (welche ja für k = 1, ..., n gilt, während mindestens ein  $\xi_k \neq 0$  ist) durch die Spezialisierung  $a \rightarrow a, x \rightarrow \xi$ .

Nach dem HILBERTschen Basissatz hat das Ideal I eine Basis  $c_1(a), \ldots, c_h$  (a). Aus 12. folgt  $b_i \equiv 0$  ( $c_1, \ldots, c_h$ ). Daraus und aus 13:

14. Satz 11. gilt auch dann, wenn man als Resultantensystem von  $F_1, \ldots, F_r$  die Polynome  $c_1$  (a), ...,  $c_h$  (a) statt der Polynome  $b_1$  (a), ...,  $b_t$  (a) nimmt.

# § 4. Erweiterung auf mehrfach-homogene Gleichungen.

Der "Hauptsatz" 11. des vorigen Paragraphen lässt sich durch "sukzessive Elimination" auf mehrfach-homogene Gleichungen ausdehnen.

Eine Form im Polynombereich  $P[x_1, ..., x_m; y_1, ..., y_n; ...; z_1, ..., z_P]$  sei ein solches Polynom aus diesem Bereich, das homogen ist sowohl in  $x_1, ..., x_m$ , als in  $y_1, ..., y_n$ , u.s.w.

Ist f eine Form, so verstehen wir unter einer eigentlichen Nullstelle von f solches Elementsystem  $\{\xi_1, \ldots, \xi_m; \eta_1, \ldots, \eta_n; \zeta_1, \ldots, \zeta_p\}$  von  $\Omega$ , für welches nicht alle  $\xi_i = 0$ , nicht alle  $\eta_i = 0$  u.s.w.

Seien nun  $F_1, \ldots, F_r$  Formen mit unbestimmten Koeffizienten  $a_1, \ldots, a_p$ . Sei  $b_1, \ldots, b_1$  ihr Resultantensystem als Formen in  $x_1, \ldots, x_m$ . Dann sind  $b_1, \ldots, b_s$  Formen in  $y_1, \ldots, y_n; \ldots; z_1, \ldots, z_p$ . Aus 11. folgt: Die notwendige und hinreichende Bedingung dafür, dass, nach Ersetzung von  $a_1, \ldots, a_q$  durch Elemente  $a_1, \ldots, a_p$  von P, die aus  $F_1, \ldots, F_r$  entstehenden Formen  $f_1, \ldots, f_r$  eine gemeinsame eigentliche Nullstelle  $X = \{\xi_1, \ldots, \xi_m, \eta_1, \ldots, \eta_n, \ldots, \zeta_1, \ldots, \zeta_p\}$  haben, ist, dass die Formen  $b_1, \ldots, b_s$  für  $a_i = a_i$  eine eigentliche gemeinsame Nullstelle  $Y = \{\eta_1, \ldots, \eta_n, \ldots, \zeta_1, \ldots, \zeta_p\}$  haben.

Damit ist die Frage nach der Existenz einer eigentlichen Nullstelle zurückgeführt auf eine gleichartige Frage, aber mit einem System von Unbestimmten  $x_1, \ldots, x_m$  weniger. Geht man so weiter, so findet man schliesslich ganzzahlige Polynome  $c_1(a), \ldots, c_t(a)$ , die das Resultantensystem des Formensystems  $F_1, \ldots, F_r$  bilden. Versteht man wie früher unter dem Resultantensystem der spezialisierten Formen  $f_1, \ldots, f_r$ , das spezialisierte Resultantensystem  $c_1(a), \ldots, c_t(a)$ , so gilt wie früher der Satz.

15. Die notwendige und hinreichende Bedingung dafür, dass die Formen  $f_1 ext{...}, f_r$  eine eigentliche gemeinsame Nullstelle in  $\Omega$  haben, ist das Verschwinden ihres Resultantensystems.

Auch jetzt sind die Polynome  $c_i$  (a) des Resultantensystems homogen in den Koeffizienten jeder einzelnen Form  $F_k$ .

# § 5. Bestimmung der Lösungen mittels der u-Resultante.

Wenn das Formensystem  $f_1, \ldots, f_r$  die eigentliche Nullstelle  $\{\xi_1, \ldots, \xi_m, \ldots, \zeta_1, \ldots, \zeta_p\}$  hat, so sind auch alle Punkte  $\{\lambda \xi_1, \ldots, \lambda \xi_m, \ldots, \nu \zeta_1, \ldots, \nu \zeta_p\}$ , wo  $\lambda \neq 0, \ldots, \nu \neq 0$ , eigentliche Nullstellen; alle diese bilden zusammen eine Nullstellenklasse.

Es habe nun das Formensystem  $f_1, \ldots, f_r$  endlichviele, etwa q Nullstellenklassen. Wir wollen für die Koordinatenverhältnisse

$$\xi_1^{(a)}: \xi_2^{(a)}: \ldots: \xi_m^{(a)}; \quad \eta_1^{(a)}: \eta_2^{(a)}: \ldots: \eta_n^{(a)}; \ldots \qquad (a=1,\ldots,q)$$

dieser Nullstellenklassen algebraische Ausdrücke herleiten.

Wir bilden zu dem Zweck mit unbestimmten Koeffizienten die Multilinearform

$$f(u) = \sum_{1}^{m} \sum_{i=1}^{n} \ldots \sum_{1}^{p} u_{ij\ldots k} x_i y_j \ldots z_k.$$

Das Resultantensystem von  $f_1, \ldots, f_r, f(u)$  sei

$$k_1(u), \ldots, k_t(u).$$

 $k_1(u), \ldots, k_t(u)$  sind Polynome in den u mit Koeffizienten aus P. Für bestimmte, dem Körper  $\Omega$  entnommene Werte  $v_{ij\ldots k}$  der Unbestimmte  $u_{ij\ldots k}$  verschwinden  $k_1(v), \ldots, k_t(v)$  dann und nur dann, wenn  $f_1, \ldots, f_r, f(v)$  eine gemeinsame eigentliche Nullstelle haben, also wenn für mindestens ein  $\alpha$ :

$$\sum_{1}^{m} \ldots \sum_{1}^{p} v_{ij\ldots k} \, \xi_{i}^{(\alpha)} \, \eta_{j}^{(\alpha)} \ldots \zeta_{k}^{(\alpha)} = 0.$$

Setzen wir also

$$f^{(a)}(u) = \sum_{1}^{m} \ldots \sum_{1}^{p} u_{ij\ldots k} \, \xi_{i}^{(a)} \, \eta_{j}^{(\alpha)} \ldots \zeta_{k}^{(a)},$$

so sind  $k_1(u), \ldots, k_t(u)$  durch alle  $f^{(\alpha)}(u)$  teilbar.

Ist nun k(u) der grösste gemeinsame Teiler von  $k_1(u),\ldots,k_t(u)$  und sind  $v_{ij\ldots k}$  Elemente von  $\Omega$  so dass k(v)=0, so muss, für mindestens ein  $a, f^{(\alpha)}(v)=0$  sein; also verschwindet das Produkt  $\prod_{i=1}^{q} f^{(\alpha)}(u)$  in allen Nullstellen des Polynoms k(u), also ist nach dem HILBERTschen Nullstellensatz 9) eine Potenz von  $\prod_{i=1}^{q} f^{(\alpha)}(u)$  durch k(u) teilbar. Daraus folgt:

16. Der grösste gemeinsame Teiler k(u) der Polynome  $k_1, (u), \ldots, k_t(u)$  hat die Gestalt:

Das Polynom k(u) soll die u-Resultante von  $f_1, \ldots, f_r$  heissen.

Diese u-Resultante ergibt nun, wenn man ihn in seine Linearfaktoren zerlegt, den gesuchten algebraischen Ausdrück für die Nullstellenklassen. Zu jeder Nullstellenklasse gehört nach (5) ein Linearfaktor von k(u) und umgekehrt; ist nun

$$f^{(a)}(u) = \sum \ldots \sum u_{ij\ldots k} \varphi_{ij\ldots k}^{(a)}$$

ein solcher Linearfaktor, so sind die Koordinatenverhältnisse der zugehörigen Nullstellenklasse eindeutig bestimmt durch die Forderung, dass

<sup>9)</sup> Siehe Fussnote 5.

die  $\varphi_{ij...k}^{(\alpha)}$  den Produkten  $\xi_i^{(\alpha)}...\zeta_k^{(\alpha)}$  proportional sein sollen. Diese Forderung führt nämlich zu den Gleichungen

$$\xi_1^{(\alpha)}: \xi_2^{(\alpha)}: \dots: \xi_m^{(\alpha)} = \varphi_{1j...k}^{(\alpha)}: \varphi_{2j...k}^{(\alpha)}: \dots: \varphi_{mj...k}^{(\alpha)}$$
 u.s.w. . . (6)

Damit ist im Falle endlichvieler Lösungsklassen das gestellte Problem erledigt. Im allgemeinen Fall kann man, die MERTENSsche Eliminationstheorie  $^{10}$ ) folgend, soviele Linearformen f(u), f(v), ... mit unbestimmten Koeffizienten hinzunehmen, dass das Resultantensystem nicht verschwindet; setzt man dann den grössten gemeinsamen Teiler gleich Null, so hat man die Gleichung der Nullstellenmannigfaltigkeiten höchster Dimension in Linien- oder Ebenen- u.s.w. Koordinaten. Wie man, nach Division durch diesen grössten gemeinsamen Teiler weitergehend, zu allen Nullstellenmannigfaltigkeiten kommen kann, hat MERTENS a.a.O. angegeben; es ist hier nicht nötig, näher darauf einzugehen.

<sup>10)</sup> F. MERTENS, Sitzungsberichte Wien 108 (1899) S. 1377 ff.

Anatomy. — "The comparative ontogenetic development of the corpus striatum in reptiles." By J. Faul. (Communicated by C. U. ARIENS KAPPERS.)

When we examine a section through the prosencephalon of the frog's brain (Fig. 1) we can at once divide the hemisphere into a dorsal or pallial part and a ventral part. The dividing lines are the zona limitans medialis and lateralis. On account of their histological structure these parts can be further subdivided into a dorso-medial part or archipallium, a dorso-lateral part or palaeopallium, a ventro-medial part or septum and a ventro-lateral part or striatal region. For the understanding of the forebrain structure in reptiles and mammals a more detailed consideration of the frog's brain is of the greatest service, as it affords us a type where the relations of the above-mentioned parts are easily discerned. In fact, the frog's brain is the prototype of the higher forms.

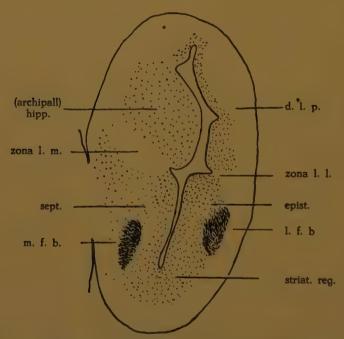


Fig. 1. Transverse section of the frogs hemisphere.

The striatum of the frog consists of two divisions: a palaeostriatum (palaeost.) ventrally and an epistriatum (epist.) laterally. The former only acquires its characteristic form on the level of the foramen Monroi near the junction of the diencephalon and prosencephalon. It has connections

with the hypothalamus and parts lower down in the brain stem. The epistriatum is so called from its position dorsal to the striatal region, but the word must not be understood in a genetic sense (as arising from the striatum proprium or palaeostriatum), for it arises from the brain wall dorsal to the striatal region, extending also more frontally than the former.

In fishes the epistriatum is much more developed especially in Ganoids and Teleosts, where the mantle is stunted and extroverted. Here it grows out further medially over the whole palaeostriatum and manifestly replaces (KAPPERS) a surface development of the pallium. This reciprocal growth of the primary epistriatum in Teleosts is especially striking in the Symbranchidae (v. d. HORST).

In support of this conception is the fact that we have only a small epistriatum in Selachians where the pallium is well developed. This is still more striking in Ceratodus, where the wall of the forebrain hardly shows any thickening, while the surface extension of the pallium is considerable. (HOLMGREN and VAN DER HORST.)

So also in Amphibia the epistriatum is small, while there is a large palaeo-pallial development, but also here the epistriatum (as in fishes) receives olfactory tract fibres (HERRICK).

In Reptilia we find additions to the striatum and pallium. The palaeostriatum is covered here dorso-laterally in its entire antero-posterior extent by a large mass attached dorso-laterally to the pallium. When EDINGER in 1896 published his work on the reptilian forebrain he described this whole body as epistriatum, deriving it from the striatum. ELLIOT SMITH (1919) described it as arising from the pallium and gave it the name hypopallium.

In his studies on the phylogenesis of the corpus striatum in 1908 KAPPERS resolved EDINGER's epistriatal ridge into an anterior and a posterior part. By studying their fibre connections he found the anterior part or neostriatum to be in connection with the dorsal thalamus that has undergone great development in comparison to the amphibian stage, the thalamus of reptiles being distinguished by two nuclei which in this form and significance do not appear in amphibia or fishes and are to be recognised as neothalamic nuclei — the nucleus anterior and the so-called nucleus rotundus.

The last mentioned is the primitive analogue of the nucleus medials and ventralis of the mammalian thalamus that contain receptive cells for a portion of the trigeminal and medial fillet and send new neurones to the forebrain. This is the thalamo-frontal tract which is in Reptiles a neostriatal connection, in fact it is responsible for the appearance of the latter.

So the neostriatum is formed (as also later the neopallium) at the same time as the nuclei of the neo-thalamus.

The posterior part of the striatum receives a large number of tertiary olfactory fibres coming from the lateral olfactory cortex and also some from the area precommissuralis septi. These olfactory fibres are therefore of a higher order than the bulbar fibres running to the epistriatum of the frog. The archipallium or hippocampal pallium occupying the dorso-medial wall

in Reptilia receives similar tertiary olfactory fibres as this part of the striatum does. On account of their similarity in these fibre connections KAPPERS called this posterior part secondary epistriatum or archistriatum. The archi- and the neo-striatum are contiguous. Only in Varanus salvator there is a fissure between them. The archistriatum is attached however mainly to the lateral cortex plate which has advanced in differentiation whereas the neostriatum joins the hemispherial wall more frontally.

Consequently the archistriatum has fibre connections just as definite as those of the neostriatum. Laterally it is connected with the tractus cortico-archistriaticus running backward from the palaeocortex and already described by EDINGER, UNGER, MEYER etc. Medially it is connected with fibres from the basi-medial grey through the taenia semicircularis and with the opposite archistriatum by the interarchistriatic commissure. Moreover it has a path of discharge into the hypothalamus and brain stem (analogous to the olfactory projection tract of CAJAL?) which arches over the crus in its passage to the hypothalamus and further backward (also observed by HERMAN, 1925).

Similar differentiations as in the striatum occur in the pallium.

With the differentiation of the archipallium or hippocampus cortex medially and the piriform or palaeo-cortex laterally the beginning of a neo-cortex may start between them. As yet, however, it is not completely free from olfactory connections, so we prefer to call it general 1) or rather dorso-lateral pallium.

The development of the striatum therefore shows the closest parallelism to that of the pallium: Where only a palaeopallium is present, as in fishes, there is also present a primary epistriatum functionally equivalent to it. Where an archipallium is developed as in Reptiles also an archistriatum develops receiving fibres of a similar nature. Lastly the neostriatum shows similarity to the early dorso-lateral or general pallium. To quote again from KAPPERS (Folia Neurobiol. 1908): "From reptiles onward a new part is added to the striatum which receives and sends out fibres not present in the lower vertebrates. The latter newly added part of the striatum bears the same relation as regards the succession of its appearance and the nature of its connections to the older striatum as the archicortex and the neocortex to the palaeocortex and can best be called archistriatum (secondary epistriatum or nucleus amygdala) and neostriatum in contradistinction to the other parts."

The palaeostriatum in reptiles has two types of cells, large more ancient cells in the centre and a small more recent type around it which moreover is first well developed in reptilia. The former, homologous to the palaeostriatum of amphibia, continues in a caudal direction in the nucleus entopeduncularis of the hypothalamus (KAPPERS) and fibres arise from it—the tractus striohypothalamicus some of which even reach the mid-brain.

<sup>1)</sup> This expression is used by Miss CROSBY, 1917.

In reptiles the palaeostriatum is enlarged (palaeostriatum augmentatum) by a mass of small cells (still more so in birds Kappers '22). This latter receives a great number of caudal fibres which are not so numerous in amphibia. This evidently ascending bundle can be followed with the above-mentioned descending bundle as a general basal bundle (Brachium ventrale or ventral peduncle) and likewise has connections with the hypothalamus and mid-brain, perhaps even with the oblongata. The whole palaeostriatum, but especially this more small-celled receptive part, has a great wealth of fibres, being the origin and receptive centre of the above-mentioned tracts as well as providing the passage for tracts to the neostriatum.

Thus the palaeostriatum is connected with ventral systems in the thalamus and mid-brain.

The neostriatum — as the neopallium — is however — in reptiles at least — connected with nuclei of the dorsal thalamus — or neothalamus. The fibres which serve the connection between the neothalamus and neostriatum form a sharply circumscribed tract above the ventral peduncle and form the brachium dorsale or dorsal peduncle.

Studying the ontogenetic development of these relations in reptiles I made use of embryological series of Sphenodon, Chrysemys picta and Varanus chlorosus, present in the embryological collection of the Anatomical Institute of the University of Amsterdam for the use of which I am greatly indebted to Professor L. Bolk. My results are as follows:

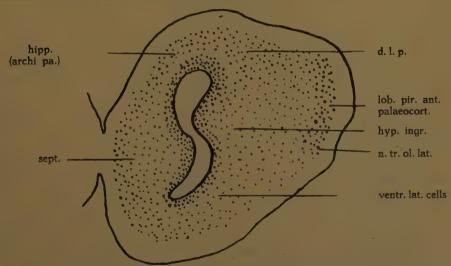


Fig. 2. Frontal section of the forebrain of Sphendon (DENDY's stage R.)

In frontal section of Sphenodon (DENDY's stage R) anteriorly we see a hypopallial ingrowth (hyp. ingr.) extending into the olfactory ventricle. Occupying the greater part of the lateral surface at the site of this swelling is the anterior clump-like mass of cells which represents the anterior end

of the piriform cortex, the ventral portion of which we may take as the origin of the nu. tr. olfactorii lateralis of CROSBY. (Fig. 2.) The hemisphere consists of a dorsal medial sector or primitive hippocampus (HIPP), a dorsolateral or general pallium, (D.L.P.) a ventro-medial septum and ventrolateral cells. Frontally the palaeostriatum is not evident but about the middle of the hemisphere all parts are clear (Fig. 3).

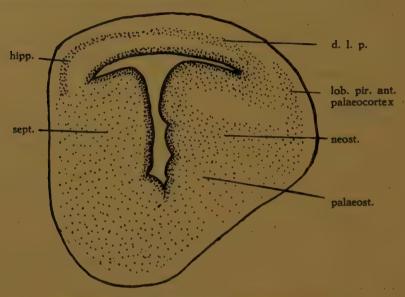


Fig. 3. Frontal section of the hemisphere of Sphenodon (behind fig. 2) DENDY's stage R.—

The dorso-medial sector consists of a uniform column of cells in the middle of the wall (HIPP); laterally, where it runs into the general pallium (D.L.P.), its cells become diffuse and can be traced down medially to the upper end of the palaeo-cortex (lob. pir. ant) into the dorsal part of the hypopallial swelling where they continue in the surface of the latter, leaving a clear area placed horizontally in this swelling opposite the middle of the piriform cortex (Fig. 3). The piriform or palaeo-cortex forms a slight bulging laterally showing more clearly its upper than its lower limit. Moreover the cells of the piriform cortex stand out clear on account of their deep staining. The septal portion is very massive (Fig. 4). The palaeostriatal cells are not so closely packed as those of the swelling above it. The palaeo-cortex, though distinct anteriorly, posteriorly runs smoothly into the general pallium showing that its differentiation has not proceeded very far (Fig. 4).

Posteriorly the fibres of the brachium collect in sufficient numbers in the base of the palaeostriatum to make themselves clear and at the junction of the diencephalon and telencephalon we notice some larger cells ventro-lateral to them (Fig. 4). Behind the junction of the diencephalon and telencephalon it comes to lie ventrally like a V-shaped mass. The

posterior portion of the dorsal striatum is the archistriatum or amygdala of KAPPERS. JOHNSTON and CROSBY have also analysed the same region in the Turtle and Alligator respectively. Both agreed that it is of an

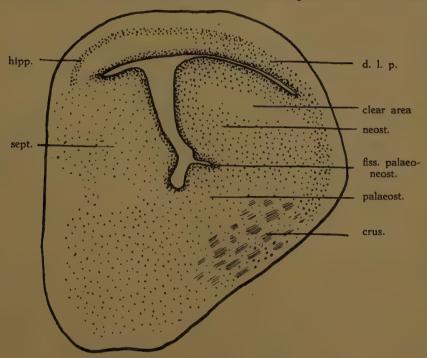


Fig. 4. Transverse section of the forebrain of Sphenodon behind fig. 3

DENDY's stage R.

olfactory character and that it finds a homologue in the nucleus amygdala of mammals. About its more minute subdivisions the opinions and nomenclature differ. At all events, it is in the most intimate relation with the nucleus tractus olfactorius lateralis.

When followed posteriorly the hollow of the V becomes filled up by a central group of cells which seem to be terminal part of the hypopallium, which extends backwards into the archistriatum. In this posterior region the intraventricular swelling has no clear area such as characterised sections through the anterior or neostriatal part, but the cells have a diffuse and scattered arrangement (Fig. 5 and 6). Lying on the ventral surface of the posterior part of the hemisphere is the olfacto-habenular tract (Fig. 5 Tr. olf. hab.) which runs medially to the side of the thalamus at the di-telencephalic junction to the habenula. The palaeostriatum is continuous with the hypothalamus (not drawn in Fig. 5 over the cruss (as is the case with the entopeduncular nucleus in amphibia), while those of the archistriatum seem to be continuous with those of the nucleus preopticus behind the palaeostriatum also over the crus.

The arrangement of the lateral pallial edge, its extension down on the medial side of the piriform lobe, foreshadows the arrangement met with

in more highly developed reptilia as shown by KAPPERS in the Lizard and by CROSBY in the Alligator.

Also Miss Hines has studied the ontogeny of the striatum in Sphenodon

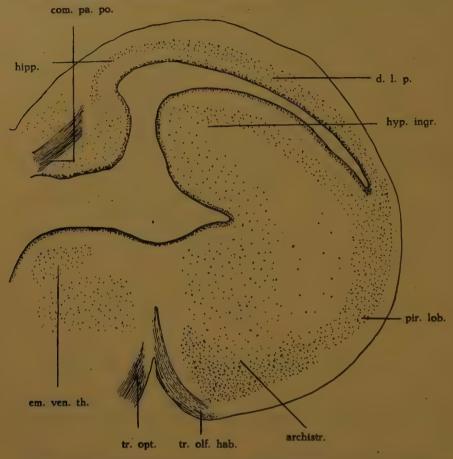


Fig. 5. Transverse section of the forebrain of Sphenodon on the level of the foramen of Monro. DENDY's stage R.

and gives a comparison of it with the completed structure. She concludes that the complete swelling is formed from a proliferation of the cells and matrix on the medial side of the piriform lobe — a growth in situ probably caused by the neurobiotactic influence of the upcoming thalamo-frontal fibres. She thinks its connection with the pallium round the pallio-striatal angle is secondary and only occurs in a late stage of embryonic development.

Whereas in Sphenodon only the dipping in of the pallium to take part in the formation of the neostriatum is readily recognisable, in Chrysemys the relations are more characteristic of what is seen in higher Reptiles.

In Chrysemys picta embryos (Fig. 7) one sees above the palaeostriatum a horizontal mass of cells above which the lateral edge of the pallium dips down into the neostriatal ridge. The former is the neostriatum, the latter the primordium neopallii in CROSBY's sense. Posteriorly the primordium

neopallii ascends till finally it becomes level with the dorso-lateral pallium (Fig. 8). The neostriatum meanwhile increases to take its place

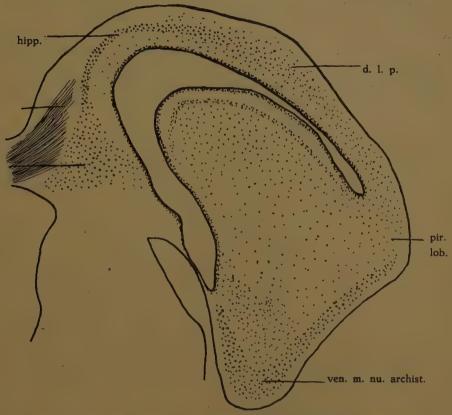


Fig. 6. Transverse section of the forebrain of Sphenodon on the level of the comm. pallii posterioris. DENDY's stage R.

in the "dorsal ventricular ridge" and just behind the junction of the primordium neopallii with the other cortex (superpositio lateralis KAPPERS) it comes into connection with the ventro-lateral edge of the latter.

The growth of the dorsal ventricular ridge, including here in that term the neostriatum and the small downgrowth of cortex, takes place from the dorso-lateral edge of the pallium at its junction with the piriform or palaeo-cortex. The growth of the neostriatum was the first to appear (as is seen also in Sphenodon). Later in phylogeny the primordium neopallii grows down into the dorso-lateral part of the anterior division of the neostriatum. At the same time the anterior end of the latter bulges frontally so that when a frontal section of this anterior part is taken, the neostriatum appears isolated whilst the primordium neopallii appears in connection with the lateral pallial edge (Fig. 7). It is only when the sections are followed antero-posteriorly that the true connections are revealed. It is then seen that the two growths projecting into the ventral projecting

edge of the primordium neopallii, and immediately behind it the neostriatum proper.

We have to thank JOHNSTON whose exhaustive researches on the brain of Chelone both in embryonic and adult preparations have illucidated these interesting relations for us. His dorsal ventricular ridge (the hypopallium of Elliot Smith) appears however to include both the neostriatum and archistriatum of Kappers as well as a connection with the primordium neopallii. When traced backward the primordium neopallii recedes upward into the dorsolateral pallium and into the caudal end of the pallium where

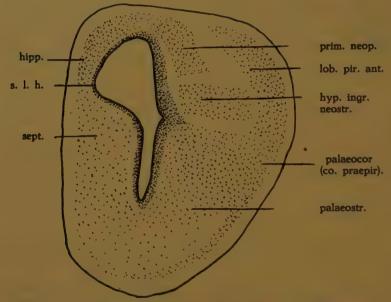


Fig. 7. Transverse section of the forebrain of an embryo of Chrysemys picta in front of the foramen Monroi.

the amygdala is clearly shown. This has led JOHNSTON at first to regard the neostriatum as a growth from the amygdala.

Also in the developed Turtle I found the neostriatum to be connected with the postero-ventral part of the piriform cortex; its point of connection with the pallium being pushed back by the growth of the primordium neopallii, that bulges in front of it.

Whereas Elliot Smith makes no distinction between the anterior and posterior parts of the hypopallium as regards this origin but calls the whole of the pallial ingrowth hypopallium, Kappers and De Lange have separated the hypopallium into an anterior neostriatum and a posterior archistriatum, finding in Varanus salvator the fissura neo-archistriatica between them. Johnston also notes that even in Sphenodon a shallow groove over the crus delineates an anterior part derived from the pallium from a posterior part derived from the piriform cortex.

With regard to the cells occupying the basal part of the forebrain, the continuity of the mesial complex with the nucleus olfactorius lateralis

can be traced. This connection was called by JOHNSTON diagonal band of BROCA. It passes obliquely across the base of the brain along the palaeocortex as a dense collection of cells and connects the medial with

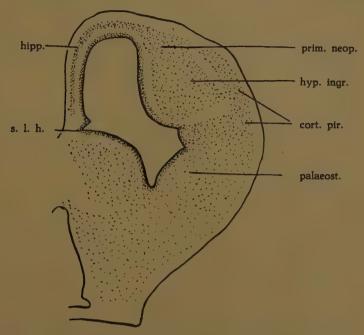


Fig. 8. Transverse section of the forebrain of an embryo of Chrysemys picta behind the foramen Monroi.

the lateral olfactory area. A similar relation was seen by KAPPERS in Varanus and by CROSBY in the Alligator.

The archistriatum as we have seen is also connected over the crus with

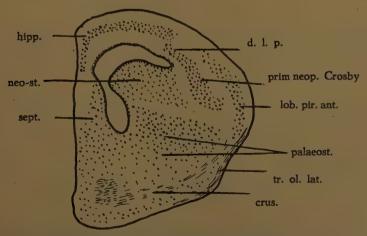


Fig. 9. Transverse section of the forebrain of an embryo of Varanus chlorosus in front of the foramen Monroi.

the nucleus preopticus by strands of cells HUBER and CROSBY's interstitial nucleus, accompanying the olfactory projection tract of CAJAL which arches over the crus to disappear in the hypothalamus and brain stem and is connected to its fellow of the opposite side by the interarchistriatic commissure which runs with the anterior commissure.

Nowhere are the boundaries and relations of the several elements of the striatum more clearly marked or show fibre connections so definitely as in Varanus salvator as described and mapped out by KAPPERS. I have convinced myself of the relations in an adult specimen of this animal. The palaeostriatum lies basally in the forebrain, being most clearly developed on the level of the foramen and connected chiefly by descending fibres (the ventral forebrain peduncle) with the hypothalamic and midbrain nuclei. Fronto-dorsally to the palaeostriatum is the neostriatum connected to the dorsal or neothalamic nuclei by a strong projection tract chiefly of ascending fibres (the dorsal forebrain peduncle).

This neostriatum is closely related to the pallium frontally and laterally, the pallium in the former situation being greatly thickened where it receives some of the fibres of the dorsal forebrain peduncle which run beyond the neostriatum together with the palliostriatal fibres found by HERMAN. The neostriatum in Varanus is, however, sharply marked off from the palaeostriatum by the fissura neo-palaeostriatica and from the archistriatum by the fissura neo-archistriatica. Finally the archistriatum is demarcated from the palaeostriatum by the fissura palaeo-archistriatica which I found to be a caudal continuation of the fissura neo-palaeostriatica. The tractus cortico-archistriaticus gathers from the palaeocortex and running backwards on the ventro-lateral surface of the hemisphere turns up and radiates in the archistriatum.

I have been able to study the ontogenetic development of these relations in another species of Varanus (chlorusus) and found the following facts.

The first of the striatum that arises is the palaeostriatum. Frontally, above the palaeostriatum we see a mass of cells bulging into the ventricular lumen (Fig. 9. neostr.). Lateral to this is a column of cells (prim. neop.) extending dorso-laterally around the palliostriatal angle into the pallium (D. L. P.). When traced posteriorly the latter mass of cells disappears altogether out of the ventricular swelling and coincides with the dorso-lateral pallium. At the same time the detached mass of cells which lies medial to it gradually increases to take its place and finally gains connection with the cortex (Fig. 10). The lateral mass of cells near the hypopallial 1) swelling in an anterior frontal section of the hemisphere contains the primordium neopallii of CROSBY (KAPPERS' superpositio lateralis), the pallial thickening of JOHNSTON in the Turtle — while the medial detached

<sup>1)</sup> ELLIOT SMITH thought that the hypopallium came from near the s. endorhinalis, JOHNSTON points out however that at the caudal end of the sulcus endorhinalis there is an invagination to form a part of the amygdaloid complex and that the hypopallium is at the posterior part of the rhinal fissure which is here pushed behind the area piriformis.

mass of cells that gains connection posteriorly with the dorso-lateral pallium apparently develops into the neostriatum of KAPPERS.

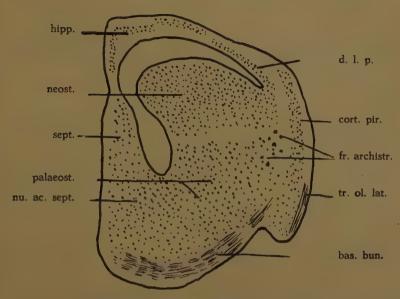


Fig. 10. Transverse section of the forebrain of an embryo of Varanus chlorusus behind fig. 9.

Behind this the main mass of the archistriatum arises, in connection with the cortex piriformis and above the palaeostriatum.

#### Resumé.

As a result of my own researches concerning the ontogenetic development of the striatal parts in reptiles I found:

- 1. The palaeostriatum arises at the junction of the telencephalic floor with the hypothalamus. The first rudiment of the striatum (palaeostriatum) appears as a thickening at this junction, not as an outgrowth from the thalamus as pretended by SPATZ.
- 2. The archistriatum arises as a thickening dorso-lateral to the palaeostriatum. It has constituents derived from the piriform and dorso-lateral pallium.
- 3. The neostriatum arises partly from the dorso-lateral pallium dorsal to the palaeostriatum and anterior to the archistriatum.
- 4. The primordium neopallii is chiefly located in front of the neostriatum.

#### LITERATURE.

ARIENS KAPPERS, C. U. 1908. Die Phylogenese des Rhinencephalons, des Corpus Striatum und der Vorderhirncommissuren. Folia Neurobiol. Bd. V.

- —— 1908. Weitere Mitteilung über die Phylogenese des Corpus Striatum und des Thalamus. An. Anz. Bd. 33.
  - --- 1921. Vergleichende Anatomie des Nervensystems Bd. 2, T. 2. Haarlem.
- —— 1922. The ontogenetic development of the Corpus Striatum in birds, and a comparison with mammals and man. These Proceedings Vol. 26.

CROSBY, Miss C. 1917. The forebrain of Alligator Mississippiensis. Journ. of Comp. Neur. Vol. 27.

DE LANGE, S. T. 1911. Das Vorderhirn der Reptilien. Folia Neurobiol. Bd. V.

-- 1913. Das Zwischenhirn und das Mittelhirn der Reptilien. Fol. Neur. Bd. VII.

— 1913. L'évolution phylogénétique du Corps Strié: Le Névraxe.

DE VRIES, E. 1910. Das Corpus Striatum der Säugetiere. An. Anz. Bd. 37.

EDINGER, 1896. Neue Studien über das Vorderhirn der Reptilien. Abh. Senckenb. Ges. Bd. 19, Frankfurt.

HERMAN, W. 1925. The relations of the striatum and the pallium in Varanus, Brain. Vol. 48, Part 3, 1925.

HERRICK, C. J. 1910. The morphology of the Forebrain in Amphibia & Reptilia. Journ. Comp. Neur. Vol. 20.

- 1921a. A Sketch of the origin of the cerebral hemispheres. Journ. Comp. Neur. Vol. 32.
- —— 1921b. The Connections of the Vomero-Nasal Nerve, accessory olfactory bulb and amygdala in Amphibia. Journ. Comp. Neur. Vol. 33.

HINES, MARION Miss 1922. Studies on Growth and differentiation of the Telencephalon in Man. Journ. Comp. Neur. Vol. 35.

—— 1923. The Telencephalon in Sphenodon Punctatum. Journ. Comp. Neur. Vol. 35. HOLMGREN, NILS 1922. Points of view concerning forebrain morphology in lower vertebrates. Journ. Comp. Neur. Vol. 34.

HOLMGREN N. and C. J. VAN DER HORST. Contribution to the Morphology of the brain of Ceratodus. Acta Zoologica. Bnd. 6, 1925.

HORST, C. J. VAN DER 1920. The forebrain of the Symbranchidae. Proceedings of the Kon. Akademie v. Wetensch. Amsterdam.

HUBER and CROSBY. On thalamic and tectal nuclei and fiber paths in the brain of the american Alligator. Journ. Comp. Neur. Vol. 40, 1926.

JOHNSTON, T. B. 1915b. The cell masses in the forebrain of the Turtle Cestudo Carolina. Journ. Comp. Neur. Vol. 25.

- —— 1916. Evidence of a motor pallium in the forebrain of Reptiles. Journ. Comp. Neur. Vol. 26.
- —— 1916. The development of the dorsal ventricular ridge in Turtles. Journ. Comp. Neur. Vol. 26.
- 1923. Further Contributions to the study of the evolution of the forebrain. Journ. Comp. Neur. Vol. 35.
- —— 1923. Further contributions to the study of the evolution of the forebrain. Survey of forebrain morphology. Journ. Comp. Neur. Vol. 36.

SHELLSHEAR, J. L. 1920. The basal arteries of the forebrain and their functional significance. Jour. of Anat. Vol. 55.

SMITH, G. ELLIOT 1910. Harris and Gale lecture. The Lancet.

- -- 1917. The Nervous System in Cunningham's Anatomy.
- —— 1919. A preliminary note on the morphology of the corpus striatum and the origin of the neopallium.

SPATZ. Ueber Beziehungen zwischen der Substantia nigra des Mittelhirns und dem Globus pallidus des Linsenkerns. Erg. Heft zum Anat. Anzeiger Bnd. 55, 1922.

Mathematics. — "Ueber Schnitte von Punktmengen". By W. HUREWICZ. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of January 30, 1926).

Sei E ein topologischer Raum, über den ausser den vier Hausdorffschen Axiomen (betreffend "Existenz", "Durchschnitt", "Offenheit" und "Trennbarkeit") zunächst keine weiteren Voraussetzungen getroffen werden. Unter einem Schnitt  $\sigma$  von E verstehen wir eine Zerlegung von E in drei paarweise fremde Mengen

$$E = E_1 + E_2 + F$$
,  $E_1 \cdot E_2 = E_2 \cdot F = F \cdot E_1 = 0$ ,

wobei die Mengen  $E_1$  und  $E_2$  nicht leer sind und F als gemeinsame Begrenzung haben:

$$E_1 \neq 0$$
,  $E_2 \neq 0$ ;  $F = \overline{E}_1 \cdot E_2 + E_1 \cdot \overline{E}_2$  1)

Die Menge F nennen wir die Grenzmenge des Schnittes  $\sigma^2$ ). Von zwei Mengen sagen wir, dass sie durch  $\sigma$  getrennt seien, wenn die eine von ihnen in  $E_1$ , die andere in  $E_2$  enthalten ist.

Es sei nun  $(M_1,M_2)$  ein durch  $\sigma$  getrenntes Paar abgeschlossener Mengen. Die Gesamtheit aller Schnitte, durch die das Paar  $(M_1,M_2)$  getrennt wird, nennen wir eine Umgebung des Schnittes  $\sigma$ . Da diese Umgebungen, wie man leicht einsieht, den vier Hausdorffschen Axiomen genügen, wird durch unsere Festsetzung ein topologischer Raum  $\mathfrak E$  definiert, dessen Elemente die sämtlichen Schnitte von E bilden. Sind die Mengen E und  $E^*$  homöomorph, dann sind auch die zugehörigen Schnitträume  $\mathfrak E$  und  $\mathfrak E^*$  homöomorph. Ist der Raum E normal, so ist der Schnittraum  $\mathfrak E$  regulär  $\mathfrak I$ ). Ferner liegt, falls E normal ist, eine Menge  $\mathfrak I$  von Schnitten (als Teilmenge des topologischen Raumes  $\mathfrak E$  betrachtet) dann und nur dann in  $\mathfrak E$  dicht, wenn jedes Paar von zueinander fremden abgeschlossenen Mengen durch Schnitte aus  $\mathfrak M$  getrennt ist.

<sup>1)</sup> Mit  $\overline{M}$  bezeichnen wir die abgeschlossene Hülle der Menge M.

<sup>&</sup>lt;sup>2</sup>) Es kann natürlich mehrere Schnitte mit derselben Grenzmenge geben; z.B. gibt es in einem unendlich viele Punkte enthaltenden zusammenhangslosen Raum unendlich viele Schnitte mit leerer Grenzmenge.

<sup>&</sup>lt;sup>3)</sup> Ein topologischer Raum heisst  $regul\"{a}r$ , wenn zu jedem Punkt p und zu jeder Umgebung U von p eine Umgebung V von p existiert, die samt ihrer Begrenzung in U liegt. Ein topologischer Raum heisst normal, wenn in ihm je zwei zu einander fremde abgeschlossene Mengen in zwei fremde Gebiete eingebettet werden können. Vgl. über diese Begriffe VIETORIS Monatshefte f. Math. u. Phys. 31, 1921, S. 173, TIETZE, Math. Annalen 88, 1923, S. 301, und ALEXANDROFF und URYSOHN, Math. Annalen 92, S. 265, wo insbesondere die Bezeichnungen regulär und normal eingeführt werden.

Sei nun E ein dem zweiten  $\operatorname{Abz\"{a}hlbarkeitsaxiom}$  genügender regulärer topologischer Raum 1). Eine Menge 21 von Schnitten nennen wir ein a-System, wenn folgende Bedingung erfüllt ist: Ist  $\sigma_1, \sigma_2, \ldots, \sigma_n, \ldots$  irgend eine abzählbare Folge von Schnitten, die Elemente von U sind, und sind  $F_1, F_2, \ldots F_n, \ldots$  die zugehörigen Grenzmengen, so kommt in  $\mathfrak A$  auch jeder Schnitt vor, dessen Grenzmenge in der Summe  $F_1 + F_2 + \ldots +$  $+F_n+\ldots$  enthalten ist. Die  $\alpha$ -Systeme haben folgende wichtige Eigenschaft: Damit ein a-System U im Schnittraum & dicht liege, ist hinreichend und (natürlich auch) notwendig, dass jeder Punkt in E von jeder ihn nicht enthaltenden abgeschlossenen Menge durch Schnitte aus U getrennt sei.

Sei nun n eine ganze Zahl  $\geq -1$ . Wir bezeichnen mit  $\mathfrak{C}_n$  die Gesammtheit aller Schnitte, deren Grenzmenge im Sinne von BROUWER, MENGER und URYSOHN höchstens n-dimensional ist 2). Man kann zeigen, dass En ein a-System ist. Der Raum E ist höchstens n-dimensional, wenn in ihm jeder Punkt von jeder ihn nicht enthaltenden abgeschlossenen Menge durch Schnitte aus En-1 getrennt ist. Nach dem eben ausgesprochenen Satz ist dies gleichbedeutend mit der Aussage: Der Raum E ist dann und nur dann höchstens n-dimensional, wenn  $\mathfrak{E}_{n-1}$  in  $\mathfrak{E}$ dicht liegt 3).

Das System E<sub>-1</sub> ist in sämtlichen a-Systemen als Teil enthalten. Die Beziehung  $\mathfrak{E}_{-1} = 0$  gilt dann und nur dann, wenn E zusammenhängend ist. Die Verhältnisse vereinfachen sich, wenn der zu Grunde liegende Raum E kompakt ist und dem zweiten Abzählbarkeitsaxiom genügt 1). Dann genügt nämlich auch der Schnittraum dem zweiten Abzählbarkeitsaxiom und da er, wie wir früher sahen, regulär ist, ist er metrisationsfähig $^5$ ). Ist E bereits als metrischer Raum gegeben, so kann die Metrisation von & folgendermassen durchgeführt werden: Als Abstand zweier Schnitte  $\sigma_1$  und  $\sigma_2$  definieren wir die untere Schranke aller Zahlen r > 0, die folgende Eigenschaft haben: Zu jedem Punktepaar (a, b), das durch

<sup>1)</sup> Solche Räume sind mit separabeln metrischen Räumen äquivalent, vgl. P. URYSOHN, Math. Annalen 94, 1925, S. 309 und TYCHONOFF, Math. Ann. 35, S. 139.

<sup>2)</sup> In der Fassung von MENGER heisst die Menge M eines topologischen Raumes höchstens n-dimensional, wenn das System der Relativumgebungen in M gleichwertig ist mit einem System von Umgebungen mit höchstens (n-1)-dimensionalen Begrenzungen, wobei die leere Menge und nur diese (-1)-dimensional heisst.

<sup>3)</sup> Hinsichtlich kompakter (und noch etwas allgemeinerer) metrischer Räume wird diese Tatsache in anderer Terminologie von MENGER (Monatshefte f. Math. u. Phys. 33, 1924, S. 160) ausgesprochen und bewiesen. MENGER zeigt, dass in einem höchstens n-dimensionalen kompakten Raum "die Umgebungen mit höchstens (n-1)-dimensionalen Begrenzungen dicht liegen" in dem Sinn, dass zwischen je zwei Relativumgebungen, deren eine samt ihrer Begrenzung in der anderen enthalten ist, eine Relativumgebung mit höchstens (n-1)dimensionaler Begrenzung sich einschalten lässt. Diese Tatsache ergibt sich auch unmittelbar aus der Äquivalenz der BROUWERschen und der MENGER-URYSOHNschen Dimensionsdefinition.

<sup>4)</sup> Solche Räume sind mit kompakten metrischen Räumen äquivalent, vgl. URYSOHN a.a.O.

<sup>5)</sup> Vgl. die unter 1) Zitierten Arbeiten.

einen der beiden Schnitte  $\sigma_1$ ,  $\sigma_2$  getrennt ist, gibt es ein durch den anderen Schnitt getrenntes Punktepaar (a',b'), so dass d(a,a') < r, d(b,b') < r, wobei d(a,a') und d(b,b') die Abstände in E bezeichnet. Man zeigt leicht, dass durch diese Festsetzung tatsächlich ein separabler metrischer Raum definiert wird, der mit  $\mathfrak E$  äquivalent ist. Man kann weiter zeigen, dass dieser metrische Raum total beschränkt ist, d.h. dass er für jede reelle Zahl  $\varepsilon > 0$  in endlich viele Teile mit Durchmessern  $< \varepsilon$  zerfällt.

Mit Rücksicht auf die Separabilität von  $\mathfrak E$  ist  $\mathfrak E_{-1}$  höchstens abzählbar, denn das System  $\mathfrak E_{-1}$  enthält bei beliebigem E keines seiner Häufungselemente. Mit anderen Worten: Eine kompakte abgeschlossene metrische Menge kann auf höchstens abzählbar viele Arten in zwei fremde abgeschlossene Teile gespalten werden.

Ein System  $\mathfrak B$  von Schnitten nennen wir ein  $\beta$ -System, wenn zugleich mit endlich vielen Schnitten  $\sigma_1, \sigma_2, \ldots \sigma_n$  auch jeder Schnitt in  $\mathfrak B$  vorkommt, dessen Grenzmenge in der Summe der Grenzmengen der  $\sigma_k$  enthalten ist. Jedes  $\alpha$ -System ist ein  $\beta$ -System, aber nicht umgekehrt. Beispielsweise ist die Gesamtheit aller Schnitte mit endlicher Grenzmenge  $^1$ ) ein  $\beta$ -System, aber im allgemeinen kein  $\alpha$ -System.

Ist E ein kompakter, dem zweiten Abzählbarkeitsaxiom genügender Raum, dann gilt die folgende Aussage: Zwei abgeschlossene Mengen  $M_1$  und  $M_2$  sind dann und nur dann durch Schnitte eines gegebenen  $\beta$ -Systemes  $\mathfrak B$  getrennt, wenn jeder Punkt von  $M_1$  von jedem Punkt von  $M_2$  durch Schnitte aus  $\mathfrak B$  getrennt ist. Ein  $\beta$ -System  $\mathfrak B$  ist dann und nur dann dicht in  $\mathfrak E$ , wenn jedes Punktepaar in E durch Schnitte aus  $\mathfrak B$  getrennt ist. Die Menge aller Punkte, die von einem gegebenen Kontinuum durch keinen Schnitt des  $\beta$ -Systemes  $\mathfrak B$  getrennt sind, ist ebenfalls ein Kontinuum. Diese Sätze können auf die MENGER-URYSOHNsche Dimensions- und Kurventheorie, und insbesondre auch auf die Theorie des Zusammenhanges angewendet werden.

<sup>&</sup>lt;sup>1)</sup> Diese Schnitte, bzw. Umgebungen mit endlichen Begrenzungen, verwendet MENGER (Math. Annalen 98, 1925, S. 279) zur Definition "regulärer Kurvenpunkte". Liegt das System dieser Schnitte in einem zusammenhängenden Raum dicht, dann spricht MENGER von einer regulären Kurve.

Mathematics. — "Über geodätische Linien in allgemeinen metrischen Räumen." By K. MENGER. (Communicated by Prof. L. E. J. BROUWER.)

(Communicated at the meeting of January 30, 1926).

1. Zwischenpunkte in metrischen Räumen. Als metrischen Raum bezeichnet man eine Menge (deren Elemente Punkte genannt werden), wenn für jedes Paar a und b von Elementen ein Abstand definiert ist, d.i. eine reelle Zahl r(a, b) = r(b, a) > 0 für  $a \neq b$  und r(a, b) = 0 für a = b, so dass für jedes Punktetripel a, b, c die Dreiecksungleichung  $r(a, b) + r(b, c) \ge r(a, c)$  besteht.

Gilt für drei unter einander verschiedene Punkte a, b, c in der Dreiecksungleichung das Gleichheitszeichen, besteht also die Relation r(a, b) + r(b, c) = r(a, c), — dann wollen wir sagen, b sei ein Zwischenpunkt von a und c, oder auch kurz: b liege zwischen a und c. Diese Ausdrucksweise ist durch folgende leicht beweisbare Relationen gerechtfertigt: 1. Wenn b zwischen a und c liegt, dann liegt b auch zwischen c und a; dagegen ist dann a kein Zwischenpunkt von b und c, und c ist kein Zwischenpunkt von a und b. 2. Liegt a zwischen a und a und a und a zwischen a und a zwischen a und a und a zwischen a zwischen

Man bestätigt ferner leicht, dass für jedes Punktepaar a und b des Raumes die Menge bestehend aus a, b und allen Punkten zwischen a und b abgeschlossen ist.

2 Konvexe Räume. Wir nennen einen metrischen Raum konvex, wenn zu jedem Paar a und b von Punkten des Raumes ein Punkt existiert, der zwischen a und b liegt 3).

<sup>1)</sup> In der Literatur dient die Metrik allgemeiner metrischer Räume vorwiegend als Hilfsmittel zum Studium von Limeseigenschaften oder von topologischen Eigenschaften (Dichtigkeits-, Zusammenhangsverhältnisse u.s.f.). Die Zwischenpunkte metrischer Räume sind dagegen etwas wirklich rein metrisches; die Eigenschaft eines Punktes, zwischen zwei anderen zu liegen, ist von der zu Grunde gelegten Metrik abhängig und kann bei Ummetrisierung des Raumes verloren gehen.

<sup>2)</sup> Zufolge der Dreiecksungleichung gibt es ja sicher zwei nicht negative Zahlen  $\delta$  und  $\varepsilon$ , so dass  $r(a,b)+r(b,d)=r(a,d)+\delta$  und  $r(b,c)+r(c,d)=r(b,d)+\varepsilon$  ist. Setzt man den Ausdruck für r(b,d) aus der zweiten Gleichung in die erste ein, so erhält man  $r(a,b)+r(b,c)+r(c,d)-\varepsilon=r(a,d)+\delta$ ; liegt nun  $\delta$  zwischen  $\delta$  und  $\delta$  und  $\delta$  zwischen  $\delta$  und  $\delta$  und

<sup>3)</sup> Wie ich gesprächsweise feststellen konnte, hat diese Präzisierung des Konvexitätsbegriffes auch Herr VIETORIS ins Auge gefasst. — Die so definierte Konvexität ist eine

Ist der konvexe Raum kompakt (d.h. besitzt jede unendliche Teilmenge des Raumes einen Häufungspunkt im Raum), dann zeigt man leicht, dass zu je zwei Punkten a und b ein Mittelpunkt existiert, d.h. ein Punkt m. so dass  $r(a, m) = r(b, m) = \frac{1}{2} r(a, b)$  gilt. Die Menge A aller Punkte des Raumes, die zwischen a und b und zugleich in einem Abstand  $\leq \frac{1}{2} r(a, b)$ von a liegen, ist nämlich abgeschlossen, enthält also einen Punkt a', dessen Abstand von a durch keinen Punkt van A übertroffen wird. Alle Punkte zwischen a' und b haben einen Abstand  $> \frac{1}{2} r(a, b)$  von a. Nun ist der Punkt a' Häufungspunkt von Punkten zwischen a' und b. (Denn angenommen, dies letztere wäre nicht der Fall, dann könnte der Abstand von a' und den Punkten zwischen a' und b nicht unter ein gewisses  $\varepsilon > 0$  sinken und ein gewisser Punkt b' zwischen a' und b hätte diesen Abstand  $\varepsilon$  von a'; da anderseits wegen der Konvexität des Raumes ein Punkt c zwischen a' und b' existiert, so erhielten wir einen Widerspruch gegen die Definition von  $\varepsilon$ ). Der Punkt a' hat einen Abstand 🚬  $\frac{1}{2}r(a,b)$  von a und ist Häufungspunkt von Punkten, die einen Abstand  $> \frac{1}{2} r(a, b)$  von a haben; also liegt a' in Abstand  $\frac{1}{2} r(a, b)$  von a und ist daher, als Zwischenpunkt von a und b, ein Mittelpunkt dieser beiden Punkte.

Eine ganz analoge Argumentation zeigt, dass in einem kompakten konvexen Raum für jedes Punktepaar a,b und für jedes  $\lambda>0$  ein Zwischenpunkt m von a und b existiert, so dass  $r(a,m)=\lambda r(b,m)$  gilt. Es können dabei sehr wohl mehrere Punkte existieren, welche mit a und b ein Teilverhältnis  $\lambda$  haben  $^1$ ), die Gesamtheit dieser Punkte aber ist für jedes Paar a und b und für jedes  $\lambda$  eine nicht-leere abgeschlossene Menge.

3. Geodätische Linien in konvexen Räumen. Man kann nun in einem kompakten konvexen Raum zwischen je zwei Punkten  $a_0$  und  $a_1$  in einfacher Weise  $^2$ ) gewisse ausgezeichnete Bögen (d. h. topologische Bilder der Strecke) bestehend aus Punkten zwischen  $a_0$  und  $a_1$  angeben, die als geodätische Bögen zwischen  $a_0$  und  $a_1$  bezeichnet werden können.

rein metrische Eigenschaft. Wird in einer Kreislinie als Abstand zweier Punkte die Länge des kürzeren Bogens zwischen den beiden Punkten festgesetzt, dann ist die Kreislinie ein konvexer Raum. Bezeichnet man dagegen als Abstand zweier Punkte deren Entfernung in der Euklidischen Ebene, dann enthält die Kreislinie zu keinem Punktepaar einen Zwischenpunkt. Offenbar kann auch für kompakte *Teil*-mengen metrischer Räume Konvexität definiert werden.

<sup>1)</sup> Etwa wenn a und b diametral gegenüberliegende Punkte einer Kugeloberfläche sind und als Abstand zweier Punkte die Länge des kleineren Bogens vom Grosskreis durch sie festgesetzt wird.

<sup>2)</sup> Etwa indem man zuerst den Mittelpunkt  $a(^{1}/_{2})$  von  $a_{0}$  und  $a_{1}$  konstruiert, sodann den Mittelpunkt  $a(^{1}/_{4})$  von  $a_{0}$  und  $a(^{1}/_{2})$  und den Mittelpunkt  $a(^{3}/_{4})$  von  $a(^{1}/_{2})$  und  $a_{1}$ , allgemein den Mittelpunkt  $a(\frac{p}{2^{n}})$ , (p=2k+1) von  $a(\frac{k}{2^{n}-1})$  und  $a(\frac{k+1}{2^{n-1}})$  und indem man schliesslich zum Limes übergeht.

Diese Bögen sind nämlich durch jede der beiden folgenden Eigenschaften charakterisiert: Sie stellen erstens die kürzesten Verbindungen von  $a_0$  und  $a_1$  dar, genauer: ihre Länge ist gleich dem Abstand von  $a_0$  und  $a_1$  und wird von der Länge jedes nicht-geodätischen Bogens übertroffen. Greifen wir zweitens irgend drei verschiedene Punkte eines geodätischen Bogens zwischen  $a_0$  und  $a_1$  heraus, so gibt es darunter stets einen, welcher Zwischenpunkt der beiden anderen ist.

Aus diesen Tatsachen folgt leicht, dass in einen kompakten konvexen Raum für jedes Paar a und b von Punkten die Menge bestehend aus den Punkten a, b und allen Punkten zwischen a und b ein Kontinuum ist. Zugleich zeigt sich, dass jeder kompakte konvexe Raum zusammenhängend und zusammenhängend im kleinen (stetig durchlaufbar) ist  $^1$ ).

Man bemerkt endlich noch eine gewisse Abgeschlossenheit des Systems aller geodätischen Bögen, welche auf folgender Tatsache beruht: Wenn  $\{g_n\}$  (n=1,2,...) ein Folge von geodätischen Bögen ist, (der Bogen  $g_n$  etwa zwischen den Punkten  $a_n$  und  $b_n$ ) und wenn die Folge im mengentheoretischen Sinn konvergiert  $a_n$ 0, dann ist  $a_n$ 0 ein geodätischer Bogen zwischen den Punkten  $a_n$ 1 und  $a_n$ 2 und  $a_n$ 3 und  $a_n$ 4 der sich im Fall  $a_n$ 5 auf diesen einen Punkt reduziert.

4. Fortsetzung von geodätischen Linien und metrisch-singuläre Punkte. Zieht man von einem Punkt a aus eine geodätische Linie nach dem Punkt b, so kann es sein, dass ein Punkt c existiert, so dass b zwischen a und c liegt. In diesem Fall lässt sich der geodätische Bogen zwischen a und b über b hinaus fortsetzen, d. d. es existiert ein geodätischer Bogen zwischen a und c, von welchem der vorliegende geodätische Bogen zwischen a und b ein Anfangssegment bildet. Zu jedem Punkt a und zu jedem von a ausgehenden geodätischen Bogen c0 existiert aber in einem kompakten konvexen Raum ein hinsichtlich a0 extremer Punkt a0 a0, über den hinaus der Bogen a0 sich von a0 aus nicht fortsetzen lässt. Dieser Punkt a0, a0 ist dann extremer Punkt für a1 geodätischen Bögen, welche ihn mit a1 verbinden. Es kann dabei der Fall eintreten, dass der Punkt a2, a3 Extrempunkt hinsichtlich jedes Punktes des Bogens a2 ist,

<sup>1)</sup> Die Konvexität eines metrischen Raumes, eine an sich rein metrische Eigenschaft, hat also immerhin topologische Eigenschaften des Raumes zur notwendigen Folge. Man kann das im Text angeführte Resultat auch in der Form aussprechen: Unter den kompakten topologischen Räumen lassen sich bloss stetig durchlaufbare so metrisieren, dass ein konvexer Raum entsteht. Es drängt sich dann die Frage auf: Durch welche topologischen Eigenschaften sind die kompakten topologischen Räume charakterisiert, welche zu konvexen Räumen metrisiert werden können? Ist stetige Durchlaufbarkeit vielleicht auch hinreichend?

<sup>&</sup>lt;sup>2)</sup> Eine Folge  $\{M_n\}$   $(n=1,\,2,\ldots)$  von Mengen heisst konvergent, wenn folgendes gilt: Ist p irgend ein Punkt, von dem jede Umgebung mit unendlich vielen Mengen  $M_n$  Punkte gemein hat, dann liegen in jeder Umgebung von p Punkte von fast allen Mengen  $M_n$ . Die Menge aller Punkte dieser Eigenschaft heisst dann der Limes der Mengenfolge  $M_n$ .

in welchem Falle wir ihn als Extrempunkt des Bogens g schlechthin bezeichnen.

Diese Tatsachen ermöglichen eine nähere Beschreibung der metrischen Verhältnisse in konvexen Räumen. Gewisse "zentrale" Punkte sind für keinen geodätischen Bogen Extrempunkte; von jedem geodätischen Bogen, welcher einen zentralen Punkt mit einem anderen Punkt des Raumes verbindet, kann ein hinreichend kleines Endstück über den zentralen Punkt hinaus fortgesetzt werden. Die Menge der nicht-zentralen Punkte des Raumes bildet eine Art Schale des Raumes, auf welcher insbesondre auch alle Fluchtpunkte des Raumes liegen, d.h. jene Punkte, welche zwischen keinem Punktepaar des Raumes liegen und daher Extrempunkte jedes geodätischen Bogens sind, auf welchem sie liegen. Betrachten wir z.B. einen Kegelkörper im dreidimensionalen Euklidischen Raum, in welchem für je zwei Punkte als Abstand ihre Euklidische Entfernung festgesetzt ist, dann besteht die Raumschale aus der Kegeloberfläche, wobei die Kegelspitze und die Punkte der Peripherie des Basiskreises Fluchtpunkte sind. Die Punkte, welche nicht Fluchtpunkte sind, liegen in jedem kompakten konvexen Raum dicht. 1).

5. Gerade in gewöhnlichen Räumen. Die geodätischen Linien eignen sich nicht nur zur Beschreibung metrischer Singularitäten, sondern man erlangt auch durch Aufstellung von Systemen immer schärferer Postulate über das Verhalten der geodätischen Linien im Kleinen und im Grossen einen naturgemässen Weg vom allgemeinen metrischen Raum zu den gewöhnlichen Räumen. <sup>2</sup>) Von Geraden kann man sprechen, wenn je zwei geodätische Linien des Raumes höchstens einen Punkt gemein haben. Zwei Punkte des Raumes bestimmen dann eindeutig eine Gerade. Gibt es zu jedem Punkt eines kompakten konvexen Raumes eine zusammenhängende Umgebung, so dass innerhalb derselben je zwei geodätische Linien höchstens einen Punkt gemein haben, während die Umgebungsbegrenzung homöomorph ist mit einer (n—1)-dimensionalen Kugel, dann ist der Raum eine n-dimensionale Mannigfaltigkeit im Sinn der kombinatorischen Topologie.

<sup>1)</sup> Da zu den Fluchtpunkten eines Raumes sicher auch alle Endpunkte in Sinne der Kurventheorie gehören (alle jene Punkte also, zu welchen beliebig kleine Umgebungen existieren, deren Begrenzungen bloss einen Punkt enthalten), so können (vgl. Math. Annalen 95, S. 285) anderseits auch die Fluchtpunkte in einem Raum dicht liegen, solange nicht Postulate über das nähere Verhalten der geodätischen Linien eingeführt werden.

<sup>&</sup>lt;sup>2</sup>) Dabei können die elementargeometrischen Begriffe (Winkel, Uebertragungen u.s.f.) und ihre Beziehungen auf den verschiedenen Schritten dieses Weges untersucht werden.

